

Supporting Information

Rapid Oxygen Tolerant Aqueous RAFT Photopolymerization in Continuous Flow Reactors

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Experimental Part

Materials

1, 3, 5-Trioxane (Trioxin, $\geq 99\%$ Sigma Aldrich), Eosin Y Disodium salt ($>99\%$, Sigma Aldrich), triethanolamine (TEtOHA, $>98\%$, TCI), triethylamine (TEA, $>99\%$ Sigma Aldrich), dimethylaniline (DMA, $> 99\%$ Sigma Aldrich), Dimethyl sulfoxide (DMSO, Ajax Chemical), N,N-Dimethylacetamide (DMAc, HPLC grade Sigma Aldrich), Deuterium oxide (D_2O , Sigma Aldrich) were used as received. N,N-Diethylacrylamide (DEAA, 99% Sigma Aldrich), N,N-Dimethylacrylamide (DMAA, 99% Sigma Aldrich), N-Hydroxyethyl acrylamide (HEAA, 97% Sigma Aldrich), 2-Hydroxyethyl acrylate (HEA, 96% Sigma Aldrich), 4-Acryloylmorpholine (NAM, 97% Sigma Aldrich), Poly(ethylene glycol) methyl ether acrylate (POEGA, Sigma Aldrich) were purified over a column of basic alumina (Ajax Chemical, AR) to remove the inhibitor. N-Isopropylacrylamide (NIPAM, Sigma Aldrich) was purified by recrystallization in hexane / toluene 70/30 (v/ v %) to remove the inhibitor. 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl] pentanoic acid (CDTPA), 4-cyanopentanoic acid dithiobenzoate (CPADB) and 2-(n-butyltrithiocarbonate)-propionic acid (BTPA) were synthesized according to literature procedures.[1, 2] 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 $> 18 \text{ m}\Omega\cdot\text{cm}^{-1}$.

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 ($\delta = 0 \text{ ppm}$), referenced to the chemical shifts of residual solvent resonances ($1H$). The multiplicities were explained 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 $1 \text{ mL}\cdot\text{min}^{-1}$ 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).

Wavelength of LED: 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.

Additional information - Results and Discussion

Preliminary studies on EY system for initiating RDRP

Deoxygenation of reactions prior to polymerization

Table S1: Polymerization conditions for aqueous RAFT photopolymerization of PDMAA under green LED irradiation.^a

Entry ^b	Time (min)	α^c (%)	$M_{n,th}^d$ (g·mol ⁻¹)	M_n^e (g·mol ⁻¹)	$\bar{D}^e$	DP_n
A1	0.5	55	11 100	15 700	1.34	105
A2	1	59	12 000	11 800	1.33	117
A3	1.5	71	14 200	14 700	1.34	139
A4	2	80	15 800	16 000	1.39	174
A5	2.5	84	16 600	16 700	1.39	186
A6	5	96	19 300	17 100	1.34	190
A7	7.5	97	19 500	18 900	1.32	192
A8	10	97	19 100	18 100	1.33	188
A9	20	96	19 200	18 200	1.39	189
A10	30	96	19 200	18 200	1.37	189
A11	40	96	19 600	18 600	1.33	193
A12	60	>99	20 300	20 000	1.26	200
A13	10	95	19 100	15 400	1.33	188
A14	20	95	19 100	20 500	1.36	188
A15	30	95	19 100	20 400	1.40	188
A16	40	95	19 100	21 200	1.39	188
A17	60	97	19 400	20 600	1.40	191

^a Experimental conditions: solvent = water; light source = green LED light ($\lambda_{max} = 530$ nm, $0.3 \text{ mW} \cdot \text{cm}^{-2}$), [DMAA] : [BTPA] : [EY] : [TetOHA] = 200 : 1 : 0.01 : 1 concentration of monomer = 4 M. ^b Sample A1-A12 are not degassed prior to polymerization; Sample A13-A17 are degassed prior to polymerization. ^c Monomer conversions when using DMAA as monomer were determined via ¹H NMR spectroscopy (D₂O) by monitoring the disappearance of the vinyl signals (6.5 – 5.5 ppm) relative to the methylene protons in the carbon backbone (1.5 – 2 ppm) and the internal standard (5.17 ppm). ^d Theoretical molecular weight was calculated using the following equation: $M_{n,th} = [M]_0/[BTPA] \times MW^{DMAA} \times \alpha + MW^{BTPA}$, where $[M]_0$, [BTPA], MW^{DMAA} , α and MW^{BTPA} correspond to the initial monomer concentration, initial BTPA RAFT agent concentration, molar mass of the monomer, conversion determined by ¹H NMR, and the molar mass of the BTPA RAFT agent, respectively. ^e Molecular weight and polydispersity ($\bar{D}$) were determined by SEC analysis calibrated to poly(methyl methacrylate) standards.

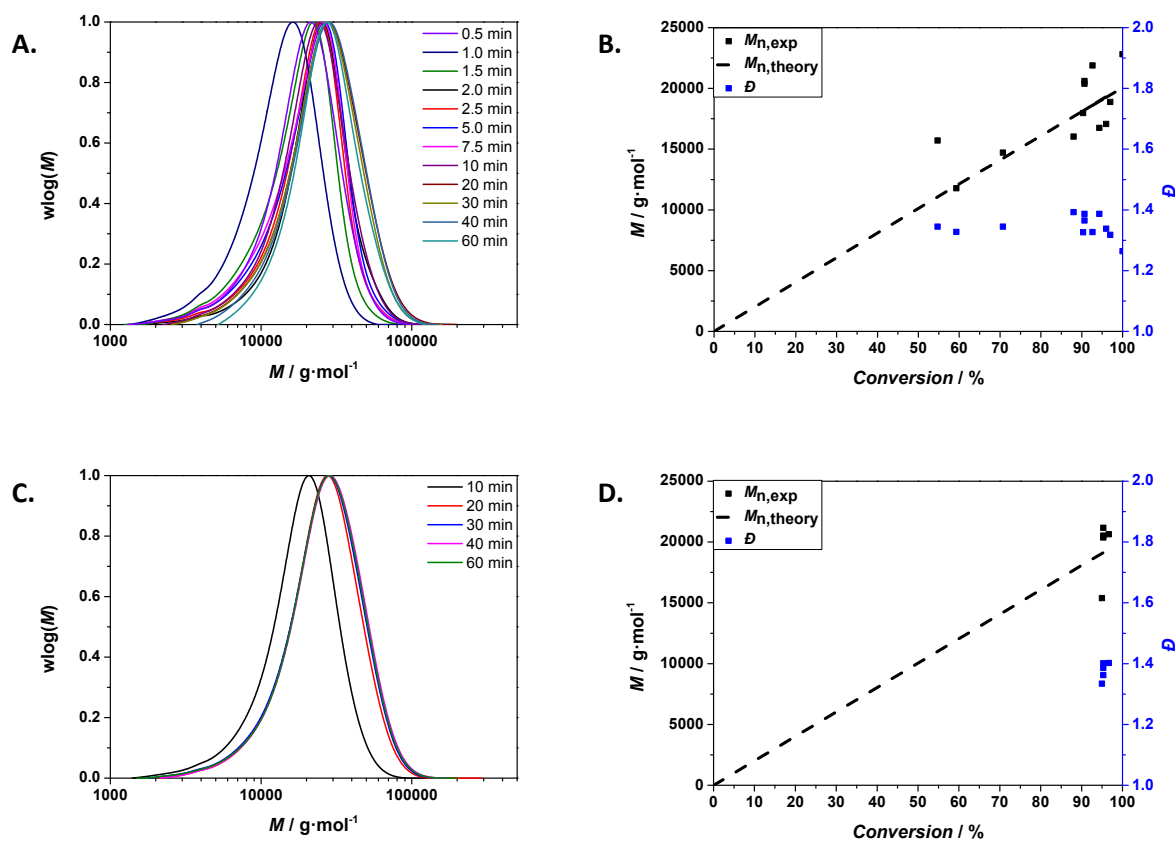


Figure S1: Polymerization kinetics of PDMAA via aqueous RAFT photopolymerization at $[\text{DMAA}] : [\text{BTPA}] : [\text{EY}] : [\text{TEtOHA}] = 200 : 1 : 0.01 : 1$. Evolution (A-C) of the molecular weight distributions versus time; (B-D) the number average molecular weight (M_n) and polymer dispersity ($\bar{D}$) with monomer conversion. (A, B) non-degassed reactions or (C, D) degassed reactions.

Concentration of TEtOHA

Table S2: Polymerization conditions for aqueous RAFT photopolymerization of PDMAA under green LED irradiation upon varying amounts of TEtOHA relative to BTPA RAFT agent.^a

Entry ^b	TEtOHA equiv.	Time min	α^c %	$M_{n,th}^d$ g·mol ⁻¹	M_n^e g·mol ⁻¹	$\bar{D}^e$	DP
B1	0.01	n.a.					
B2	0.1	0.5	30	6 200	6 800	1.29	60
B3		1.0	31	6 400	6 100	1.30	62
B4		1.5	42	8 500	6 700	1.31	83
B5		2.0	40	8 200	7 300	1.34	80
B6		2.5	48	9 800	7 900	1.31	96
B7		5.0	52	10 500	10 200	1.32	103
B8		7.5	57	11 500	11 900	1.31	113
B9		10.0	74	14 900	14 300	1.40	147
B10		15.0	76	15 300	16 500	1.31	151
B11		20.0	79	16 000	17 800	1.36	158
B12	0.5	0.5	31	6 400	7 000	1.28	62
B13		1.0	38	7 800	9 500	1.32	76
B14		1.5	42	8 600	9 900	1.32	84
B15		2.0	49	10 000	8 300	1.33	98
B16		2.5	58	11 700	9 100	1.34	115
B17		5.0	69	13 900	11 900	1.32	137
B18		7.5	75	15 100	14 300	1.34	141
B19		10.0	84	16 900	20 200	1.31	167
B20		15.0	88	17 600	17 400	1.30	174
B21		20.0	97	19 500	18 600	1.29	193
A1	1	0.5	55	11 100	15 700	1.34	109
A2		1	59	12 000	11 800	1.33	118
A3		1.5	71	14 200	14 700	1.34	140
A4		2	88	17 700	16 000	1.39	175
A5		2.5	94	18 900	16 700	1.39	186
A6		5	96	19 300	17 100	1.34	190
A7		7.5	97	19 500	18 900	1.32	192
A8		10	97	19 100	18 100	1.33	188
A9		20	96	19 200	18 200	1.39	189
A10		30	96	19 200	18 200	1.37	189
A11		40	96	19 600	18 600	1.33	193
A12		60	>99	20 300	20 000	1.26	200
B22	2	0.5	65	13 100	15 100	1.31	128
B23		1.0	68	13 700	16 000	1.29	134
B24		1.5	70	14 100	15 500	1.29	138
B25		2.0	75	15 100	17 000	1.27	148
B26		2.5	75	15 100	12 800	1.34	148
B27		5.0	78	15 700	13 300	1.31	154
B28		7.5	81	16 300	15 000	1.34	160
B29		10.0	87	17 500	17 000	1.37	172
B30		15.0	94	18 900	18 700	1.42	186
B31		20.0	>99	20 300	19 100	1.46	200

^a Experimental conditions: solvent = water; light source = green LED light ($\lambda_{max} = 530$ nm, 0.3 mW·cm⁻²), [DMAA] : [BTPA] : [EY] = 200 : 1 : 0.01 with a total concentration of monomer = 4 M. ^b Sample B1 0.01 equiv. TEtOHA; sample B2-B11 0.1 equiv. TEtOHA; sample B12-B21 0.5 equiv. TEtOHA; sample B22-B31 2 equiv. TEtOHA

relative to [BTPA]. ^c Monomer conversions when using DMAA as monomer were determined via ¹H NMR spectroscopy (D₂O) by monitoring the disappearance of the vinyl signals (6.5 – 5.5 ppm) relative to the methylene protons in the carbon backbone (1.5 – 2 ppm) and the internal standard (5.17 ppm). ^d Theoretical molecular weight was calculated using the following equation: $M_{n,th} = [M]_0/[BTPA] \times MW^{DMAA} \times \alpha + MW^{BTPA}$, where $[M]_0$, [BTPA], MW^{DMAA} , α and MW^{BTPA} correspond to the initial monomer concentration, initial BTPA RAFT agent concentration, molar mass of the monomer, conversion determined by ¹H NMR and the molar mass of the BTPA RAFT agent respectively. ^e Molecular weight and polydispersity ($\mathcal{D}$) were determined by SEC analysis calibrated to poly(methyl methacrylate) standards.

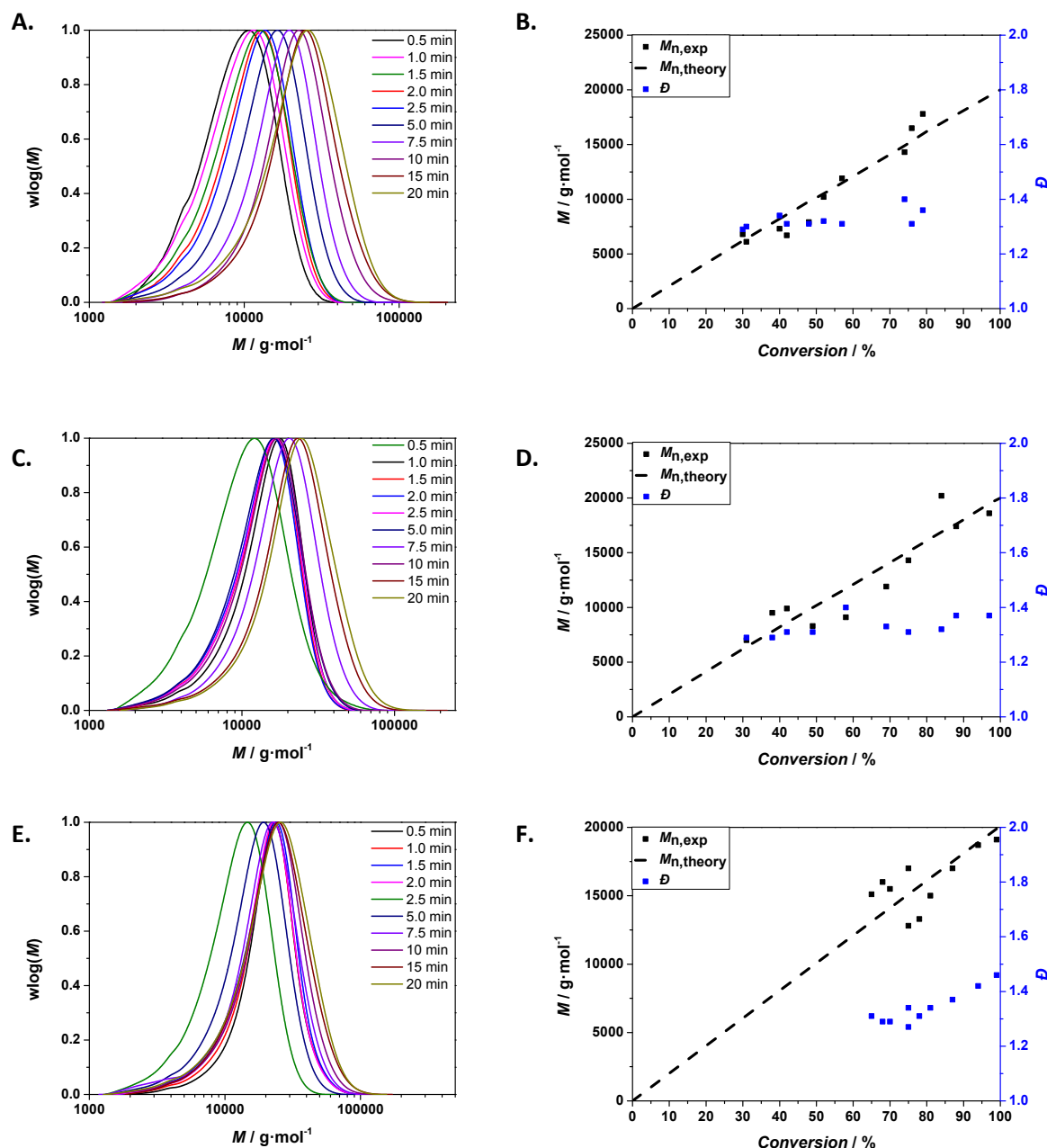


Figure S2: Polymerization kinetics of PDMAA via aqueous RAFT photopolymerization (non-degassed reactions) at [DMAA] : [BTPA] : [EY] : [TetOHA] = 200 : 1 : 0.01 : x. Evolution of (A-C-E) of the molecular weight distributions versus time; (B-D-F) the number average molecular weight (M_n) and polymer dispersity ($\mathcal{D}$) with monomer

conversion. (A, B) [BTPA] : [TEtOHA] = 1 : 0.1 or (C, D) [BTPA] : [TEtOHA] = 1 : 0.5 or (E, F) [BTPA] : [TEtOHA] = 1 : 2.

Variation in type of amine

Table S3: Polymerization conditions for aqueous RAFT photopolymerization of DMAA under green LED irradiation upon varying types of amine.^a

Entry ^b	Amine type	Time min	α^c %	$M_{n,th}^d$ g·mol ⁻¹	M_n^e g·mol ⁻¹	$\bar{D}^e$	DP
C1	TEA	0.5	47	9 800	9 300	1.41	66
C2	TEA	1	38	7 600	7 600	1.41	74
C3	TEA	1.5	42	8 700	8 400	1.42	82
C4	TEA	2	47	9 700	9 500	1.40	95
C5	TEA	2.5	56	11 300	9 800	1.39	110
C6	TEA	5.0	70	14 100	16 300	1.40	138
C7	TEA	7.5	79	15 900	18 200	1.38	156
C8	TEA	10.0	84	16 900	18 800	1.37	166
C9	TEA	15.0	97	19 500	20 600	1.43	193
C10	TEA	20.0	>99	20 300	21 000	1.47	200
A1	TEtOHA	0.5	55	11 100	15 700	1.34	109
A2	TEtOHA	1	59	12 000	11 800	1.33	118
A3	TEtOHA	1.5	71	14 200	14 700	1.34	140
A4	TEtOHA	2	88	17 700	16 000	1.39	175
A5	TEtOHA	2.5	94	18 900	16 700	1.39	186
A6	TEtOHA	5	96	19 300	17 100	1.34	190
A7	TEtOHA	7.5	97	19 500	18 900	1.32	192
A8	TEtOHA	10	97	19 100	18 100	1.33	188
A9	TEtOHA	20	96	19 200	18 200	1.39	189
A10	TEtOHA	30	96	19 200	18 200	1.37	189
A11	TEtOHA	40	96	19 600	18 600	1.33	193
A12	TEtOHA	60	>99	20 300	20 000	1.26	200
C11	DMA	60	No polymerization				

^a Experimental conditions: solvent = water; light source = green LED light ($\lambda_{max} = 530$ nm, 0.3 mW·cm⁻²), [DMAA] : [BTPA] : [EY] : [amine] = $200 : 1 : 0.01 : 1$ with a total concentration of monomer = 4 M. ^b Sample C1-C10 using TEA; sample A1-A12 using TEtOHA; sample C11 using DMA. ^c Monomer conversions when using DMAA as monomer were determined via ¹H NMR spectroscopy (D₂O) by monitoring the disappearance of the vinyl signals ($6.5 - 5.5$ ppm) relative to the methylene protons in the carbon backbone ($1.5 - 2$ ppm) and the internal standard (5.17 ppm). ^d Theoretical molecular weight was calculated using the following equation: $M_{n,th} = [M]_0/[BTPA] \times MW^{DMAA} \times \alpha + MW^{BTPA}$, where $[M]_0$, [BTPA], MW^{DMAA} , α and MW^{BTPA} correspond to the initial monomer concentration, initial BTPA RAFT agent concentration, molar mass of the monomer, conversion determined by ¹H NMR and the molar mass of the BTPA RAFT agent respectively. ^e Molecular weight and polydispersity ($\bar{D}$) were determined by SEC analysis calibrated to poly(methyl methacrylate) standards.

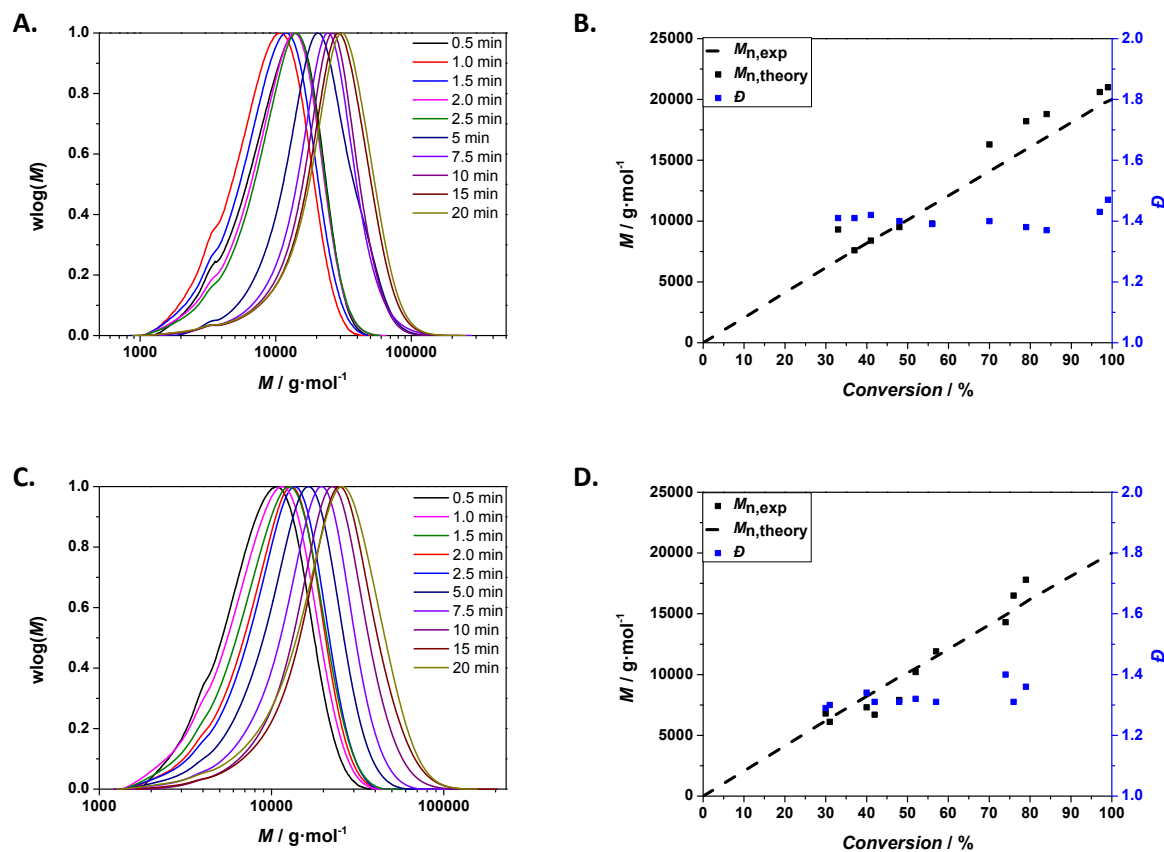


Figure S3: Polymerization kinetics of PDMAA via aqueous RAFT photopolymerization (non-degassed reactions) at $[\text{DMAA}] : [\text{BTPA}] : [\text{EY}] : [\text{amine}] = 200 : 1 : 0.01 : 1$. Evolution of (A-C) the molecular weight distributions versus time; (B-D) the number average molecular weight (M_n) and polymer dispersity ($\bar{D}$) versus monomer conversion using (A, B) triethylamine or (C, D) triethanolamine as reducing agent.

Concentration of EY

Table S4: Polymerization conditions for aqueous RAFT photopolymerization of PDMAA under green LED irradiation upon varying amounts of EY.^a

Entry ^b	<i>Eosin Y</i> equiv.	Time min	α^c %	$M_{n,th}^d$ g·mol ⁻¹	M_n^e g·mol ⁻¹	$\bar{D}^e$	DP
D1	0.005	0.5	31	6 500	6 100	1.41	63
D2		1	36	7 100	6 900	1.39	69
D3		1.5	37	8 400	7 100	1.37	81
D4		2	46	9 100	7 400	1.34	89
D5		2.5	47	9 600	10 200	1.34	94
D6		5.0	68	13 700	11 400	1.30	135
D7		7.5	74	14 800	14 600	1.31	145
D8		10.0	81	16 300	16 300	1.32	160
D9		15.0	89	17 900	18 400	1.35	147
D10		20.0	98	19 600	19 800	1.39	193
A1	0.01	0.5	55	11 100	15 700	1.34	109
A2		1	59	12 000	11 800	1.33	118
A3		1.5	71	14 200	14 700	1.34	140
A4		2	88	17 700	16 000	1.39	175
A5		2.5	94	18 900	16 700	1.39	186
A6		5	96	19 300	17 100	1.34	190
A7		7.5	97	19 500	18 900	1.32	192
A8		10	97	19 100	18 100	1.33	188
A9		20	96	19 200	18 200	1.39	189
A10		30	96	19 200	18 200	1.37	189
A11		40	96	19 600	18 600	1.33	193
A12		60	>99	20 300	20 000	1.26	200
D11	0.05	0.5	31	6 200	7 000	1.37	68
D12		1	35	7 400	8 200	1.32	80
D13		1.5	38	7 800	9 100	1.35	89
D14		2.0	46	9 100	10 400	1.33	101
D15		2.5	52	10 600	10 100	1.36	84
D16		5.0	59	12 000	10 800	1.39	118
D17		7.5	75	15 100	14 100	1.32	149
D18		10.0	82	16 800	15 200	1.40	165
D19		15.0	84	17 200	16 300	1.48	170
D20		20.0	85	17 200	18 700	1.52	170

^a Experimental conditions: solvent = water; light source = green LED light ($\lambda_{max} = 530$ nm, 0.3 mW·cm⁻²), [DMAA] : [BTPA] : [TEtOHA] = $200 : 1 : 1$ with a total concentration of monomer = 4 M. ^b Sample D1-D10 EY 0.005 equiv.; sample A1-A12 EY 0.01 equiv.; sample D11-D20 using EY 0.05 equiv.; ^c Monomer conversions when using DMAA as monomer were determined via ¹H NMR spectroscopy (D₂O) by monitoring the disappearance of the vinyl signals ($6.5 - 5.5$ ppm) relative to the methylene protons in the carbon backbone ($1.5 - 2$ ppm) and the internal standard (5.17 ppm). ^d Theoretical molecular weight was calculated using the following equation: $M_{n,th} = [M]_0/[BTPA] \times MW^{DMAA} \times \alpha + MW^{BTPA}$, where $[M]_0$, [BTPA], MW^{DMAA} , α and MW^{BTPA} correspond to the initial monomer concentration, initial BTPA RAFT agent concentration, molar mass of the monomer, conversion determined by ¹H NMR and the molar mass of the BTPA RAFT agent respectively. ^e Molecular weight and polydispersity ($\bar{D}$) were determined by SEC analysis calibrated to poly(methyl methacrylate) standards.

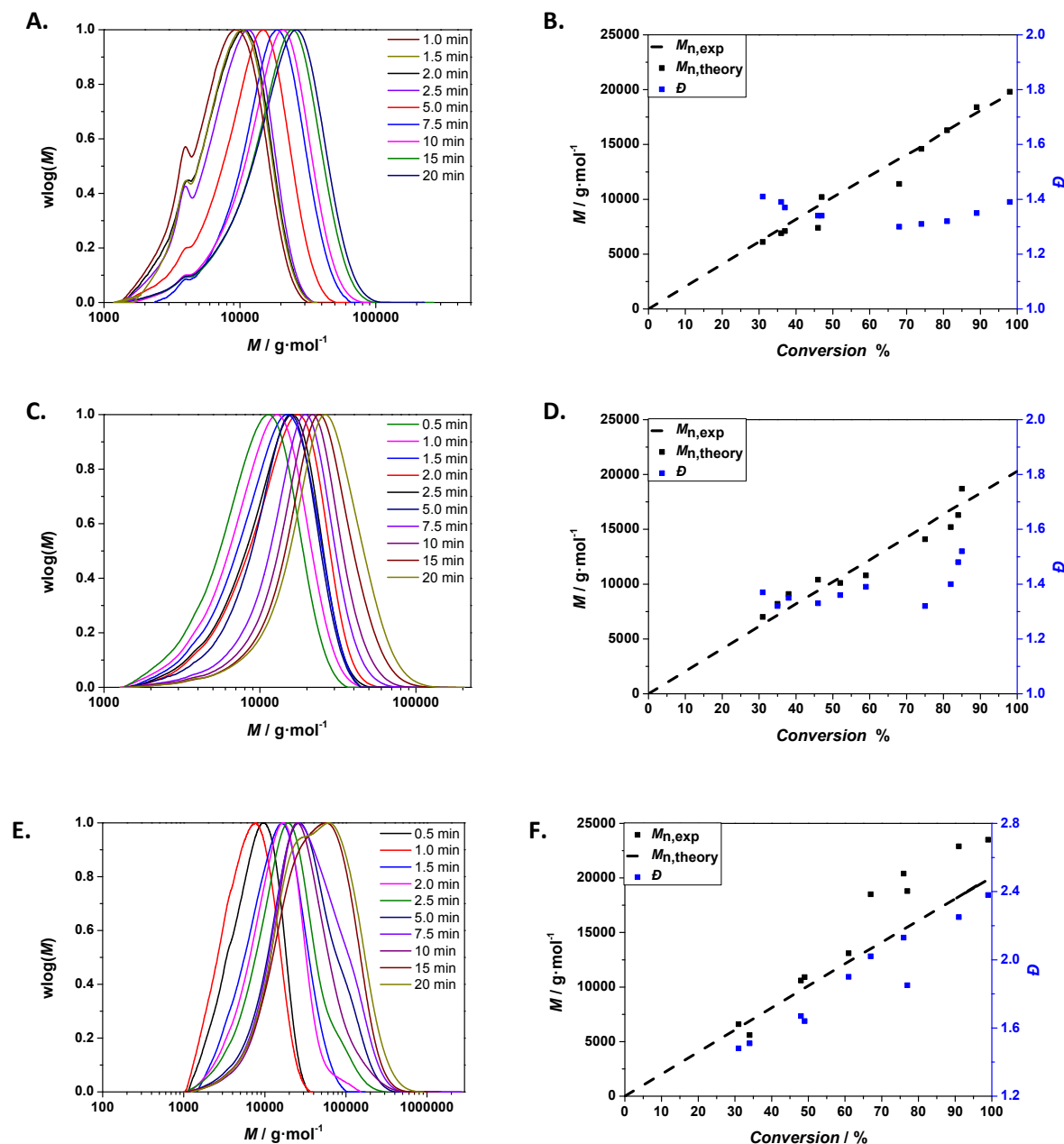


Figure S4: Polymerization kinetics of PDMAA via aqueous RAFT photopolymerization (non-degassed reactions) at $[\text{DMAA}] : [\text{BTPA}] : [\text{EY}] : [\text{TetOHA}] = 200 : 1 : x : 1$. Evolution (A-C-E) of the molecular weight distributions versus time; (B-D-F) the number average molecular weight (M_n) and polymer dispersity ($\bar{D}$) with monomer *conversion. (A, B) $[\text{BTPA}] : [\text{EY}] = 1 : 0.005$ or (C, D) $[\text{BTPA}] : [\text{EY}] = 1 : 0.05$. (E, F) $[\text{BTPA}] : [\text{EY}] = 1 : 0.01$.

Variation in type of RAFT agent

Table S5: Polymerization conditions for aqueous RAFT photopolymerization of PDMAA under green LED irradiation upon varying types of RAFT agent.^a

Entry ^b	RAFT agent	Time min	α^c %	$M_{n,th}^d$ g·mol ⁻¹	M_n^e g·mol ⁻¹	$\bar{D}^e$	DP
E1	CDTPA	0.5	31	6 100	6 600	1.48	59
E2		1	34	7 100	5 600	1.51	69
E3		1.5	48	9 900	10 600	1.67	88
E4		2	49	10 000	10 900	1.64	97
E5		2.5	61	12 500	13 100	1.90	123
E6		5.0	67	13 700	18 500	2.02	134
E7		7.5	76	15 400	20 400	2.13	151
E8		10.0	77	15 600	18 800	1.85	153
E9		15.0	91	18 300	22 900	2.25	180
E10		20.0	>99	19 900	23 500	2.38	197
E11	CDTPA	2	51	10 500	10 500	1.77	113
E12		2.5	71	14 500	17 200	2.00	142
E13		5.0	79	16 100	18 100	2.12	158
E14		7.5	79	16 100	16 800	1.47	158
E15		10.0	74	15 000	21 900	2.00	147
E16		15.0	96	19 400	22 800	1.80	190
E17		20.0	96	19 600	21 700	1.79	193
E18	CDTPA	n.a.					
E19	CDTPA	n.a.					
A1	BTPA	0.5	55	11 100	15 700	1.34	109
A2		1	59	12 000	11 800	1.33	118
A3		1.5	71	14 200	14 700	1.34	140
A4		2	88	17 700	16 000	1.39	175
A5		2.5	94	18 900	16 700	1.39	186
A6		5	96	19 300	17 100	1.34	190
A7		7.5	97	19 500	18 900	1.32	192
A8		10	97	19 100	18 100	1.33	188
A9		20	96	19 200	18 200	1.39	189
A10		30	96	19 200	18 200	1.37	189
A11		40	96	19 600	18 600	1.33	193
A12		60	99	20 000	20 000	1.26	197
E20	CPADB	60		No polymerization			

^a Experimental conditions: solvent = water; light source = green LED light ($\lambda_{max} = 530$ nm, $0.3 \text{ mW} \cdot \text{cm}^{-2}$), [DMAA] : [RAFT agent] : [EY] : [TtOHA] = 200 : 1 : 0.01 : 1 with a total concentration of monomer = 4 M. ^b Sample E1-E10 using CDTPA at $0.3 \text{ mW} \cdot \text{cm}^{-2}$; sample E11-E17 using CDTPA at $0.15 \text{ mW} \cdot \text{cm}^{-2}$; sample E18 using CDTPA at $0.3 \text{ mW} \cdot \text{cm}^{-2}$ without TtOHA; sample E19 using CDTPA at $0.3 \text{ mW} \cdot \text{cm}^{-2}$ without TtOHA and EY; sample A1-A12 using BTPA at $0.3 \text{ mW} \cdot \text{cm}^{-2}$; sample E20 using CPADB at $0.3 \text{ mW} \cdot \text{cm}^{-2}$. ^c Monomer conversions when using DMAA as monomer were determined via ¹H NMR spectroscopy (D₂O) by monitoring the disappearance of the vinyl signals (6.5 – 5.5 ppm) relative to the methylene protons in the carbon backbone (1.5 – 2 ppm) and the internal standard (5.17 ppm). ^d Theoretical molecular weight was calculated using the following equation: $M_{n,th} = [M]_0/[RAFT] \times MW^{DMAA} \times \alpha + MW^{RAFT}$, where $[M]_0$, [RAFT], MW^{DMAA} , α and MW^{RAFT} correspond to the initial monomer concentration, initial RAFT agent concentration, molar mass of the monomer, conversion determined by ¹H NMR and the molar mass of the RAFT agent respectively. ^e Molecular weight and polydispersity ($\bar{D}$) were determined by SEC analysis calibrated to poly(methyl methacrylate) standards.

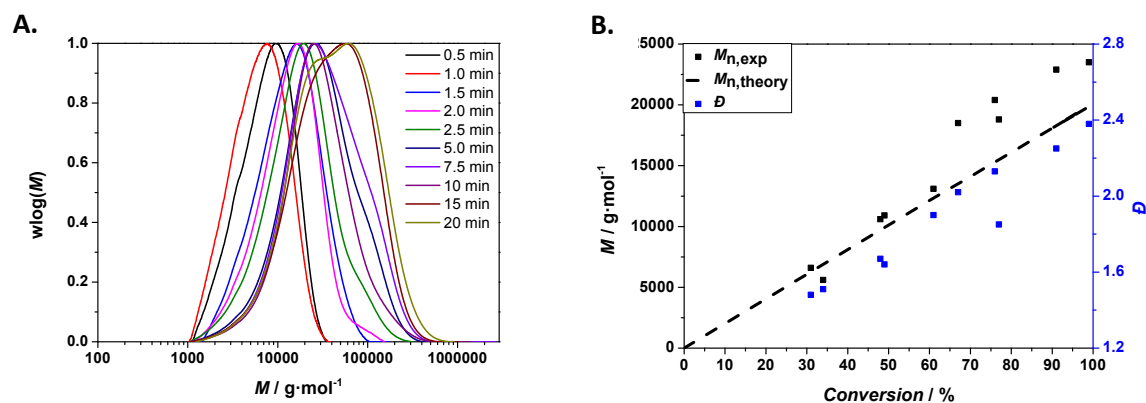


Figure S5: Polymerization kinetics of PDMAA via aqueous RAFT photopolymerization (non-degassed reactions) at [DMAA] : [CDTPA] : [EY] : [TEtOHA] = 200 : 1 : 0.01 : 1. Evolution (A) of the molecular weight distributions versus time; (B) the number average molecular weight (M_n) and polymer dispersity ($\bar{D}$) with monomer conversion at a light intensity of $0.3 \text{ mW} \cdot \text{cm}^{-2}$.

Variation in light intensity

Table S6: Polymerization conditions for aqueous RAFT photopolymerization of PDMAA under green LED irradiation upon varying light intensity.^a

Entry ^b	Intensity $\text{mW} \cdot \text{cm}^{-2}$	α^c %	$M_{n,\text{th}}^d$ $\text{g} \cdot \text{mol}^{-1}$	M_n^e $\text{g} \cdot \text{mol}^{-1}$	$\bar{D}^e$	DP
F1	0.286	83	8 500	7 900	1.33	83
F2	0.248	78	8 000	8 000	1.33	78
F3	0.210	74	7 500	7 800	1.33	73
F4	0.172	63	6 400	7 400	1.32	61
F5	0.135	65	6 600	7 500	1.31	64
F6	0.095	56	5 700	7 000	1.32	55
F7	0.057	34	3 600	6 500	1.33	34

^a Experimental conditions: solvent = water; light source = green LED light ($\lambda_{\text{max}} = 530 \text{ nm}$), [DMAA] : [BTPA] : [EY] : [TEtOHA] = 100 : 1 : 0.01 : 1 with a total concentration of monomer = 4 M and a polymerization time of 2.5 minutes; ^b Sample F1-F7 was executed at optimum reaction conditions under varying light intensity. ^c Monomer conversions when using DMAA as monomer were determined via ^1H NMR spectroscopy (D_2O) by monitoring the disappearance of the vinyl signals (6.5 – 5.5 ppm) relative to the methylene protons in the carbon backbone (1.5 – 2 ppm) and the internal standard (5.17 ppm). ^d Theoretical molecular weight was calculated using the following equation: $M_{n,\text{th}} = [M]_0 / [\text{BTPA}] \times \text{MW}^{\text{DMAA}} \times \alpha + \text{MW}^{\text{BTPA}}$, where $[M]_0$, [BTPA], MW^{DMAA} , α and MW^{BTPA} correspond to the initial monomer concentration, initial BTPA RAFT agent concentration, molar mass of the monomer, conversion determined by ^1H NMR and the molar mass of the BTPA RAFT agent respectively. ^e Molecular weight and polydispersity ($\bar{D}$) were determined by SEC analysis calibrated to poly(methyl methacrylate) standards.

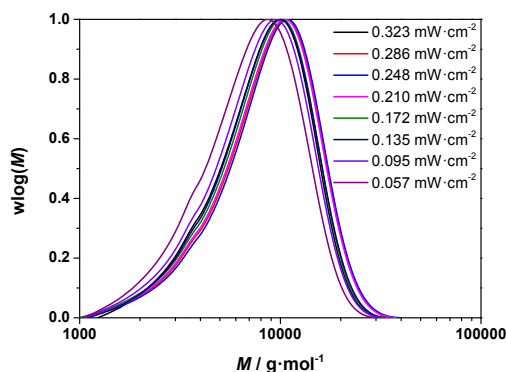


Figure S6: Polymerization kinetics of PDMAA via aqueous RAFT photopolymerization (non-degassed reactions) at [DMAA] : [BTPA] : [EY] : [TetOHA] = 200 : 1 : 0.01 : 1 showing the evolution of the molecular weight distributions upon varying light intensities.

Variation in targeted degree of polymerization

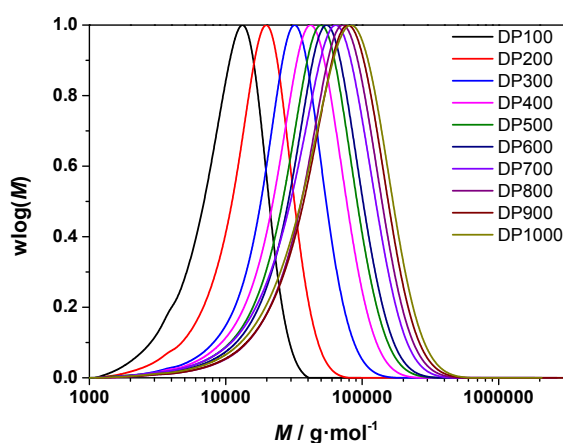


Figure S7: Polymerization of PDMAA via aqueous PET-RAFT polymerization (non-degassed reactions) at [DMAA] : [BTPA] : [EY] : [TetOHA] = variable : 1 : 0.01 : 1 with a residence time of 10 minutes, showing the evolution of the molecular weight distributions upon varying degree of polymerizations at full conversions.

Concentration of DMAA monomer

Table S7: Polymerization conditions for aqueous RAFT photopolymerization of PDMAA under green LED irradiation upon varying monomer concentrations.^a

Entry ^b	[M] mol·L ⁻¹	Time min	α^c %	$M_{n,th}^d$ g·mol ⁻¹	M_n^e g·mol ⁻¹	$\bar{D}^e$	DP
G1	4	2.5	76	15 400	15 400	1.41	153
G2	3	2.5	76	15 300	16 900	1.38	150
G3	2	2.5	81	16 300	17 600	1.38	160
G4	1	2.5	77	15 200	15 800	1.43	149
G5	0.5	2.5	91	18 200	13 000	1.43	179

^a Experimental conditions: solvent = water; light source = green LED light ($\lambda_{\text{max}} = 530 \text{ nm}$, $0.3 \text{ mW} \cdot \text{cm}^{-2}$), [DMAA] : [BTPA] : [TEtOHA] : [EY] = 200 : 1 : 1 : 0.01 for all samples; ^b sample G1 [M] = 4 M; sample G2 [M] = 3 M; sample G3 [M] = 2 M; sample G4 [M] = 1 M; sample G5 [M] = 0.5 M. ^c Monomer conversions when using DMAA as monomer were determined via ¹H NMR spectroscopy (D₂O) by monitoring the disappearance of the vinyl signals (6.5 – 5.5 ppm) relative to the methylene protons in the carbon backbone (1.5 – 2 ppm) and the internal standard (5.17 ppm). ^d Theoretical molecular weight was calculated using the following equation: $M_{n,\text{th}} = [M]_0 / [\text{BTPA}] \times \text{MW}^{\text{DMAA}} \times \alpha + \text{MW}^{\text{BTPA}}$, where $[M]_0$, [BTPA], MW^{DMAA} , α and MW^{BTPA} correspond to the initial monomer concentration, initial BTPA RAFT agent concentration, molar mass of the monomer, conversion determined by ¹H NMR and the molar mass of the BTPA RAFT agent respectively. ^e Molecular weight and polydispersity ($\mathcal{D}$) were determined by SEC analysis calibrated to poly(methyl methacrylate) standards

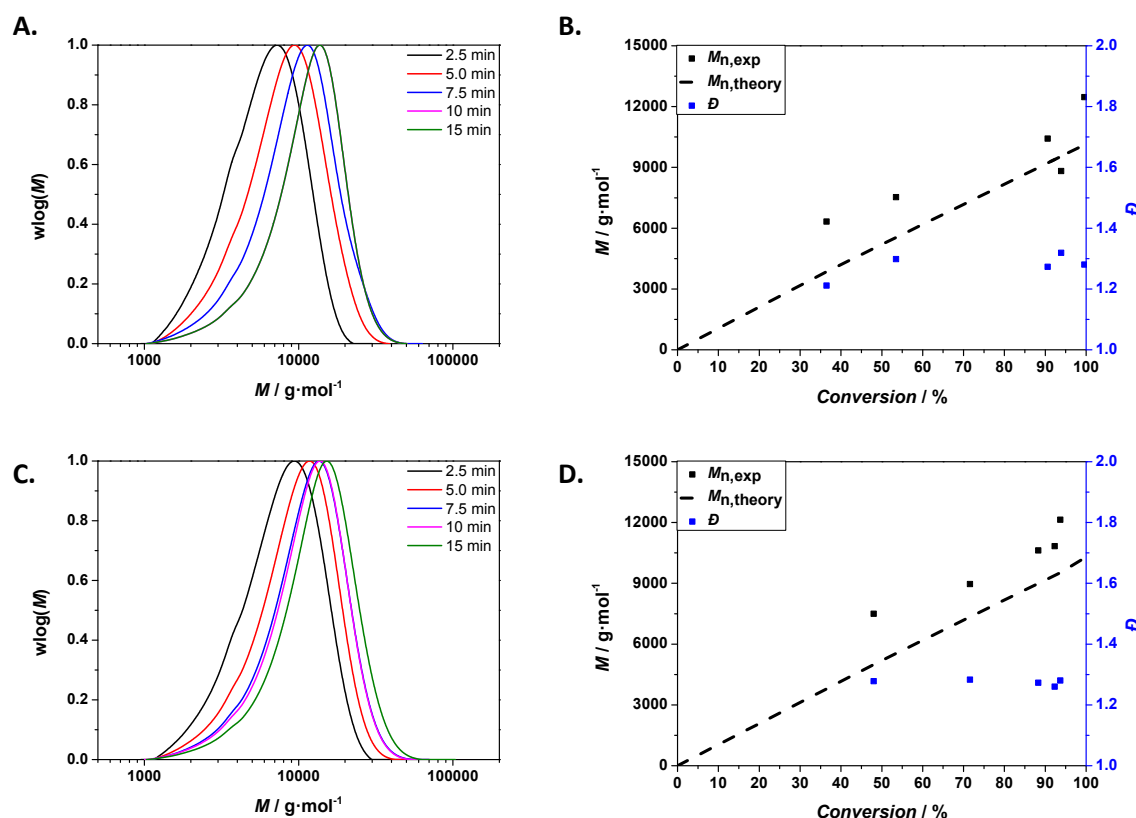


Figure S8: Polymerization kinetics of PDMAA via aqueous RAFT photopolymerization (non-degassed reactions) at [DMAA] : [BTPA] : [EY] : [TEtOHA] = 200 : 1 : 0.01 : 1. Evolution (A-C) of the molecular weight distributions versus time; (B-D) the number average molecular weight (M_n) and polymer dispersity ($\mathcal{D}$) with monomer conversion. (A, B) [M] = 2.5 M or (C, D) [M] = 4 M.

Versatility of the flow protocol

4-acryloylmorpholine (NAM)

Table S8: Polymerization conditions for aqueous RAFT photopolymerization of PNAM under green LED irradiation upon varying reaction types and reaction times.^a

Entry ^b	Reaction type	Time min	α^c %	$M_{n,th}^d$ g·mol ⁻¹	M_n^e g·mol ⁻¹	$\bar{D}^e$	DP
I1	Flow	1	9	2 700	11 100	1.52	23
I2		2	22	6 300	11 600	1.51	60
I3		3	40	11 400	12 400	1.49	110
I4		4	52	15 000	13 400	1.46	146
I5		5	67	19 100	14 700	1.44	187
I6		6	79	22 600	15 200	1.43	222
I7		7	89	25 300	15 900	1.41	249
I8		8	90	25 800	16 500	1.41	254
I9		9	96	27 400	16 900	1.41	270
I10		10	99	28 200	17 300	1.41	278
I11	batch	1	4	1 500	11 500	1.51	14
I12		2.5	13	3 900	12 300	1.55	37
I13		5	22	6 300	11 200	1.49	61
I14		10	43	12 200	13 100	1.42	118
I15		15	64	18 400	15 200	1.39	180
I16		20	82	23 500	17 800	1.33	230
I17		30	86	24 600	17 800	1.33	242
I19		45	99	28 200	19 400	1.33	278
I20		60	98	28 000	19 500	1.34	276
I21	flow	0.5	12	3 600	10 900	1.51	33
I22		1	13	3 900	11 200	1.51	36
I23		2	17	5 100	11 500	1.50	48
I24		3	15	4 600	11 600	1.51	43
I25		4	18	5 300	11 700	1.52	50

^a Experimental conditions: solvent = water; light source = green LED light ($\lambda_{max} = 530$ nm, 0.3 mW·cm⁻²), [NAM] : [BTPA] : [TtOHA] : [EY] = $200 : 1 : 1 : 0.01$ with a total concentration of monomer = 4 M. ^b Samples I1-I10 were synthesized in flow; samples I11-I20 were synthesized in batch; samples I21-I25 were synthesized in flow upon collection of sample before reaching steady state reaction conditions. ^c Monomer conversions when using NAM as monomer were determined via ¹H NMR spectroscopy (D₂O) by monitoring the disappearance of the vinyl signals ($6.5 - 5.5$ ppm) relative to the internal standard (5.17 ppm). ^d Theoretical molecular weight was calculated using the following equation: $M_{n,th} = [M]_0/[BTPA] \times MW^{NAM} \times \alpha + MW^{BTPA}$, where $[M]_0$, [BTPA], MW^{NAM} , α and MW^{BTPA} correspond to the initial monomer concentration, initial BTPA RAFT agent concentration, molar mass of the monomer, conversion determined by ¹H NMR and the molar mass of the BTPA RAFT agent respectively. ^e Molecular weight and polydispersity ($\bar{D}$) were determined by SEC analysis calibrated to poly(methyl methacrylate) standards.

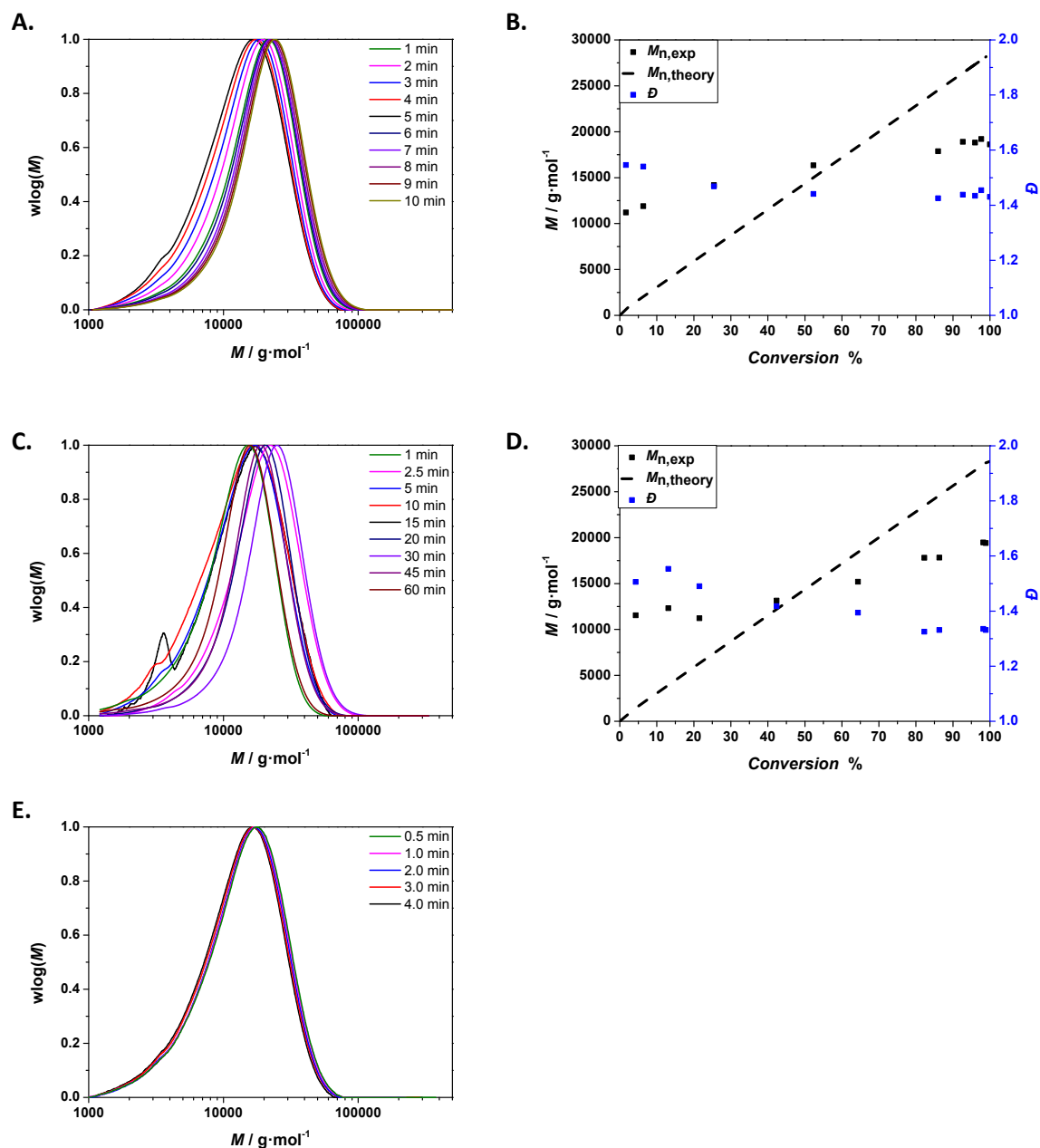
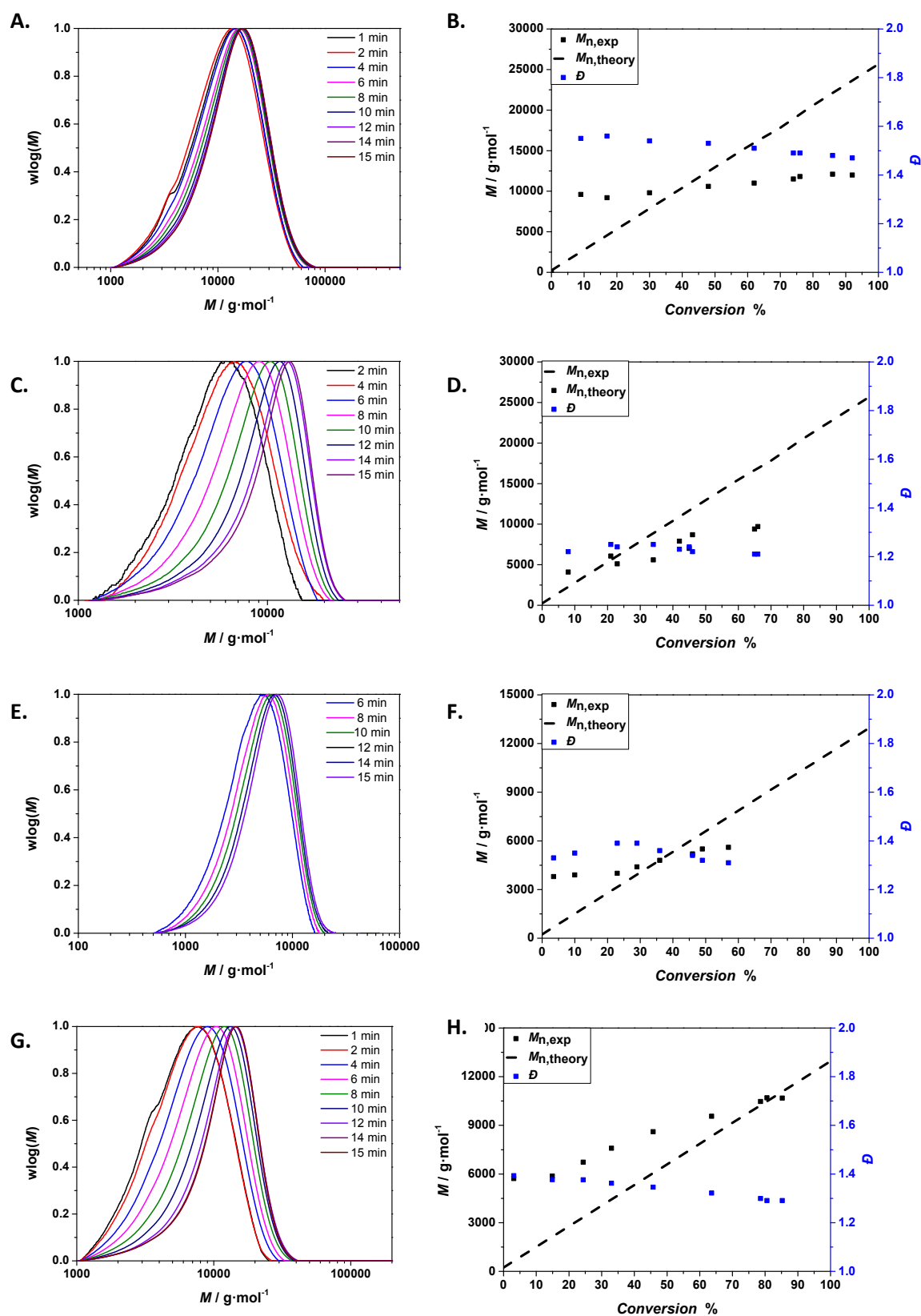


Figure S9: Polymerization kinetics of PNAM via aqueous RAFT photopolymerization (non-degassed reactions) at $[\text{NAM}] : [\text{BTPA}] : [\text{EY}] : [\text{TEtOHA}] = 200 : 1 : 0.01 : 1$. Evolution (A-C-E) of the molecular weight distributions versus time; (B-D) the number average molecular weight (M_n) and polymer dispersity ($\bar{D}$) with monomer conversion. (A, B) reactions performed in flow or (C, D) reactions performed in batch or; (E) reactions performed in flow before reaching steady state conditions.

Diethylacrylamide (DEAA)



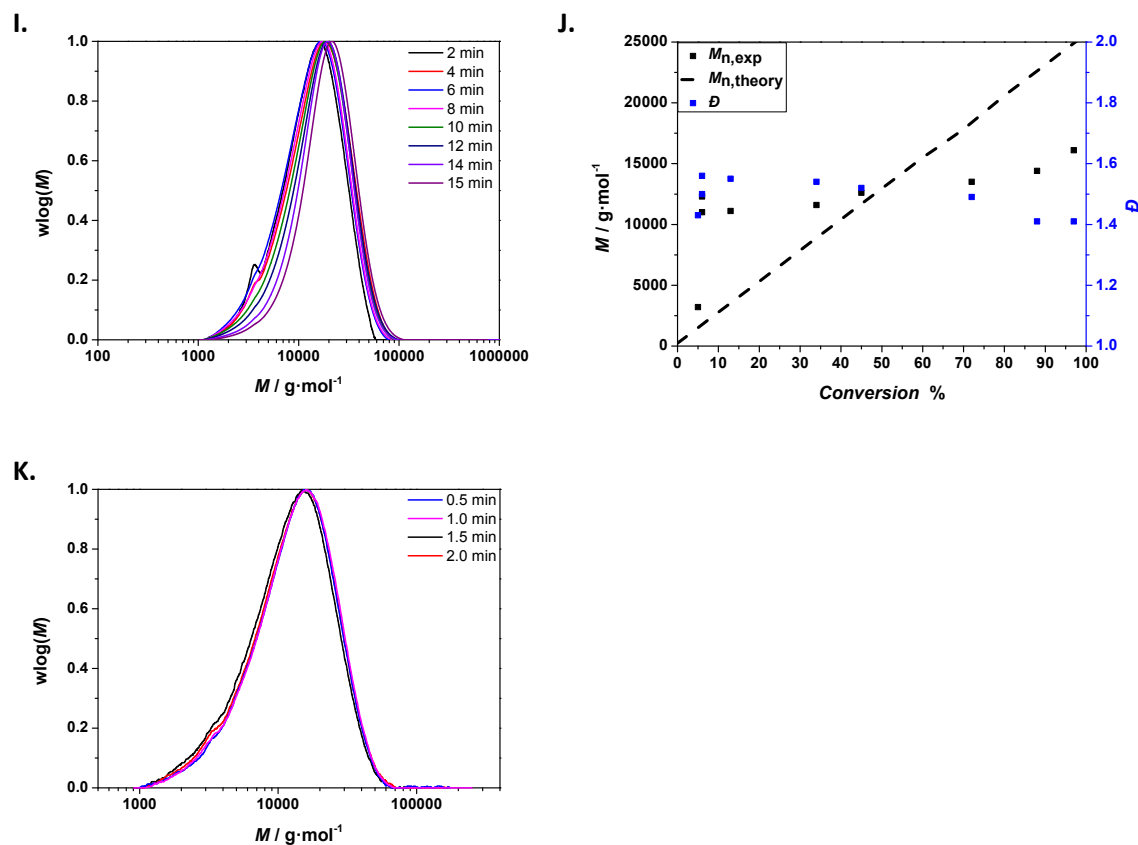


Figure S10: Polymerization kinetics of PDEAA via aqueous RAFT photopolymerization (non-degassed reactions). Evolution (A-C-E-G-I-K) of the molecular weight distributions versus time; (B-D-F-H-J) the number average molecular weight (M_n) and polymer dispersity ($\bar{D}$) with monomer conversion. (A, B) $[M] = 4 \text{ M}$ at $[\text{DEAA}] : [\text{BTPA}] : [\text{EY}] : [\text{TEtOHA}] = 200 : 1 : 0.01 : 1$ reactions performed in flow or (C, D) 4 M at $[\text{DEAA}] : [\text{BTPA}] : [\text{EY}] : [\text{TEtOHA}] = 200 : 1 : 0.01 : 1$ reactions performed in flow adding 10 v/v% of DMSO or (E, F) 4 M at $[\text{DEAA}] : [\text{BTPA}] : [\text{EY}] : [\text{TEtOHA}] = 100 : 1 : 0.01 : 1$ reactions performed in flow or (G, H) 2 M at $[\text{DEAA}] : [\text{BTPA}] : [\text{EY}] : [\text{TEtOHA}] = 100 : 1 : 0.01 : 1$ reactions performed in flow or (I, J) $[M] = 4 \text{ M}$ at $[\text{DEAA}] : [\text{BTPA}] : [\text{EY}] : [\text{TEtOHA}] = 200 : 1 : 0.01 : 1$ reactions performed in batch or (K) $[M] = 4 \text{ M}$ at $[\text{DEAA}] : [\text{BTPA}] : [\text{EY}] : [\text{TEtOHA}] = 200 : 1 : 0.01 : 1$ reactions performed in flow with sample collection before reaching steady state reaction conditions.

Tri-Block copolymer synthesis via a multistep continuous process

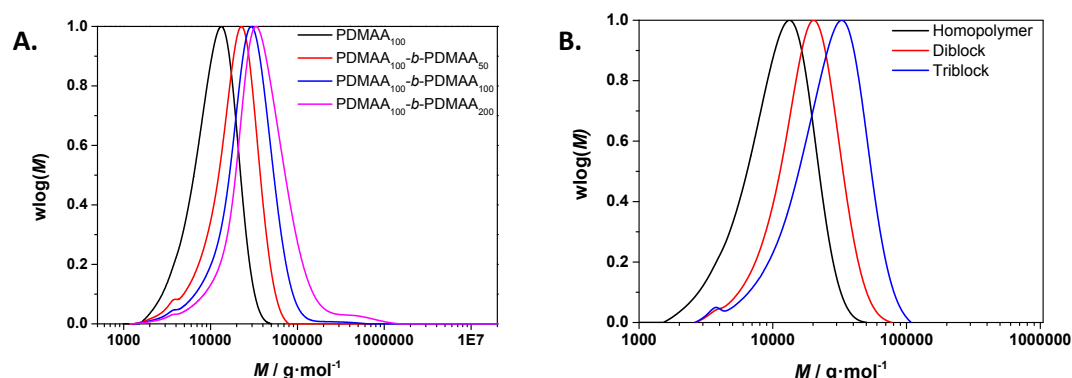


Figure S11: (A) PDMAA-*b*-PDMAA block copolymer synthesis via aqueous RAFT photopolymerization (non-degassed reactions) at $[\text{DMAA}] : [\text{PDMAA}] : [\text{EY}] : [\text{TEtOHA}] = x : 1 : 0.01 : 1$. Evolution of the molecular weight distributions upon varying degree of polymerizations (DP50, DP100 and DP200); (B) PDMAA-*b*-PDMAA-*b*-PDMAA multiblock copolymer (DP200) synthesis via aqueous RAFT photopolymerization (non-degassed reactions). Evolution of the molecular weight distributions upon chain extension of the homopolymer (DP100) and block copolymer (DP150) respectively.

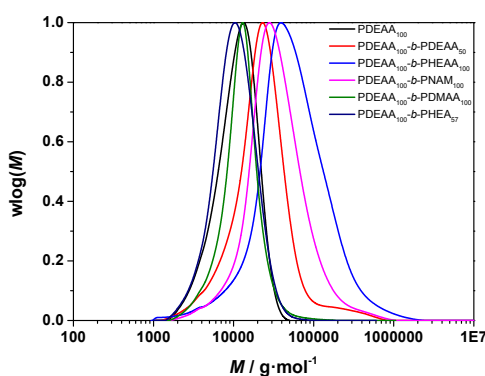


Figure S12: Block copolymer synthesis via aqueous RAFT photopolymerization (non-degassed reactions) at $[\text{M}] : [\text{macroRAFT}] : [\text{EY}] : [\text{TEtOHA}] = 100 : 1 : 0.01 : 1$. Evolution of the molecular weight distribution upon PDEAA chain extension with DMAA, DEAA, HEAA, NAM and HEA.

Additional References

1. Liu, L., et al., *pH-Triggered Polypeptides Nanoparticles for Efficient BODIPY Imaging-Guided Near Infrared Photodynamic Therapy*. *ACS Appl. Mater. Interfaces*, **2016**. 8(14) 8980-90.
2. Shanmugam, S., J. Xu, and C. Boyer, *Utilizing the electron transfer mechanism of chlorophyll a under light for controlled radical polymerization*. *Chem. Sci.*, **2015**. 6 p. 1341-1349.