Supporting Information

Hydrophobic NIR Photocatalysts for High-Throughput Aqueous RAFT Polymerization: Achieving Ultrahigh Molecular Weights with 4-ppm Dye Colloids

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Table of Contents

1. Experimental

1.1 Materials

Zinc phthalocyanine (ZnPc, 97%) was purchased from Bidepharm (China). Zinc 2,11,20,29-tetra-*tert*-butyl−2,3-naphthalocyanine (ZnTtBNc) was provided by Prof. Yongjia Shen from the East China University of Science and Technology (Shanghai, China). Brij 98 (average M_n~1150 g mol^{-1}) was purchased from J&K Scientific (China). Lithium bromide (LiBr, 99.9%), coumarin-3-carboxylic acid (CCA, 98%), and 3,3′-(anthracene-9,10-diyl) dipropanoic acid (ADPA, 95%) were purchased from Aladdin (China). *N*,*N*-dimethylacrylamide (DMA, 99%), *N*-acryloylmorpholine (NAM, 97%), poly(ethylene glycol) methyl ether acrylate (PEGA, M_n = 480 g mol^{-1}), and poly(ethylene glycol) methyl ether methacrylate (PEGMA, M_n = 500 g mol^{-1}) were purchased from Sigma-Aldrich (China). All monomers were purified by passing through a basic alumina oxide column to remove the inhibitor prior to use. 4-((((2-Carboxyethyl)thio)carbonothioyl)thio)-4-cyanopentanoic acid (CTPA, 95%) was purchased from Laajoo (China). D_2O (99.9% D), hydroquinone (99%), and *N*,*N*-dimethylformamide (DMF, >99.9%) were purchased from Energy-Chemical (China).

1.2 Characterization

Nuclear magnetic resonance (NMR) spectra were recorded using either a Bruker (Germany) Avance II 500 (500 MHz) or a Zhongke-Niujin (China) AS400 (400 MHz) instrument at room temperature using D_2O as the solvent. Chemical shifts were reported using solvent residue as the reference.
Gel permeation chromatography (GPC) measurements were conducted on an Agilent 1260 Infinity II system equipped with a Shodex guard column (P8514-KD000DMF), two Shodex separation columns (KD-803and KD-805), an Optilab refractive index detector (Wyatt Technology Corporation) and an 8-angle laser light scattering detector (Wyatt DAWN8, Wyatt Technology Corporation). HPLC grade DMF (containing 1.75 mg mL^{-1} LiBr) was used as the eluent (0.75 mL min^{-1} at 40 ^{o}C). All polymer samples were unpurified and tested directly after drying in a vacuum oven.
Transmission electron microscopy (TEM) was carried out on a JEOL JEM−2100F (Japan) at an acceleration voltage of 120 kV.
UV-visible absorption spectroscopy was conducted on an Ocean Optics DH-mini (China) at ambient temperature.
Fluorescence spectroscopy was conducted on a Shimadzu RF-5301 (Japan) at ambient temperature.
Oxygen concentration was measured using a FireSting-O_2 probe (Pyro Science, Germany) coupled with a TDIP15 temperature sensor. Data acquisition and analysis were conducted using the FireSting-O_2 Oxygen Logger software.
The emission spectra of the NIR light sources were recorded using the Ocean Optics DH-mini, and their light intensities were determined by a solar power meter SM206-SOLAR (Shenzhen Sanpo Instrument, China).

1.3 Procedures for the preparation of ZnPc and ZnTtBNc particles

Colloidal particles were prepared by dissolving the hydrophobic photocatalyst and Brij 98 in DMF, followed by addition of this solution into phosphate buffer (0.2 M, pH 5.7). Taking the preparation of ZnPc particles as an example: Brij 98 (100 mg) and ZnPc (0.07 mg) were fully dissolved in DMF (200 μL). This DMF solution was then added dropwise into 10 mL of phosphate buffer (0.2 M, pH 5.7), resulting in a pale blue, transparent colloidal solution.

1.4 Procedure for polymerizations in 96-well plates using NIR photocatalyst particles

Taking the synthesis of $PDMA_{500}$ using ZnPc particles as an example: First, the phosphate buffer solution containing ZnPc particles prepared in advance was added into one well within a 96-well plate array. Subsequently, DMA solution (93.6 μL) containing CTPA ([CTPA]/[DMA] = 1:500), glucose (6.0×10^{-6} mol, 0.0011 g), and GOx (45 U, 20.0 μL of a 2250 U mL^{-1} stock solution in phosphate buffer) were added in sequence. Then, the 96-well-plate was sealed with a plastic cover and placed under NIR light irradiation. After 12 h, the 96-well plate was removed from the light source and 1.0 mg hydroquinone was added to quench the polymerization. A small aliquot was taken for analysis via ^{1}H NMR spectroscopy to determine the monomer conversion and MALLS-GPC to determine the molecular weight (M_n) and assess the dispersity (*Đ*). For the polymerizations in 96-well plates, the heating block temperature was set to 40 ^{o}C, while the measured temperature of the polymerization solution was approximately 35 ^{o}C.

1.5 Procedure for polymerization kinetics study

Polymerization kinetics studies were performed by adding the same reaction mixture to each individual well, as described in the aforementioned polymerization procedure. After reaching the prescribed irradiation time, the reaction solution in one designated well was withdrawn using a syringe, followed by addition of hydroquinone, and the polymerization was subjected to ^{1}H NMR and MALLS-GPC analyses to determine monomer conversions, M_n and *Đ*.
For “on/off" modulation, the polymerization was performed inside one well. The NIR light was turned on/ off at scheduled times. A degassed microsyringe was used to withdraw 20 μL of the polymerization solution before each light switching. All collected samples were analyzed by ^{1}H NMR spectroscopy to determine monomer conversions and MALLS-GPC to assess M_n and *Đ*.

1.6 Procedure for chain extension

Taking the synthesis of $PDMA_{350}$-*b*-$PDMA_{250}$ as an example: 200 μL of the RAFT "cocktail" ([CTPA]/[DMA] = 1:500, [ZnPc] = 4 ppm, [Brij 98] = 10 mg mL^{-1}, [GOx] = 150 U mL^{-1}, [glucose] = 20 mM) was prepared according to the general polymerization procedure described above and added into one well within a 96-well plate array. Then, the 96-well-plate was sealed with a plastic cover and placed under NIR light (λ_{max} = 730 nm; *I* = 140 mW cm^{-2}) irradiation. After 12 h, ^1H NMR monitoring revealed 70% DMA conversion. Fresh ZnPc particles, DMA, glucose and GOx were subsequently supplemented to attain the following final concentrations in the reaction mixture: [$PDMA_{350}$]/[DMA] = 1:500, [ZnPc] = 4 ppm, [GOx] = 150 U mL^{-1}, and [glucose] = 20 mM. The resealed plate was then irradiated under NIR light for an additional 12 h to get block copolymer.

2. Results and Discussion

2.1 Construction of enzyme-NIR cascade catalysis

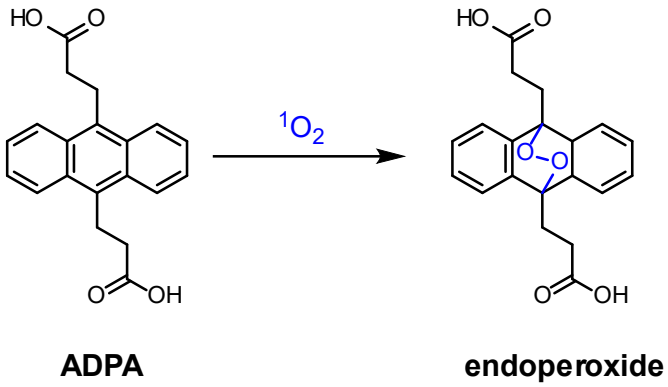

Figure S1. The mechanism of ADPA for the detection of $^1O_2$.

2.2 High-throughput RAFT Polymerizations using ZnPc particles

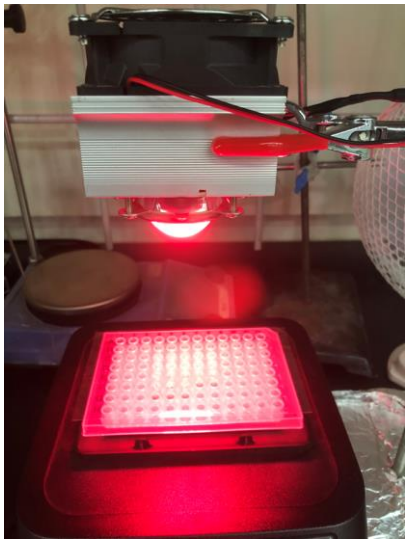

Figure S2. The experimental setup for high-throughput NIR photocontrolled RAFT polymerization.

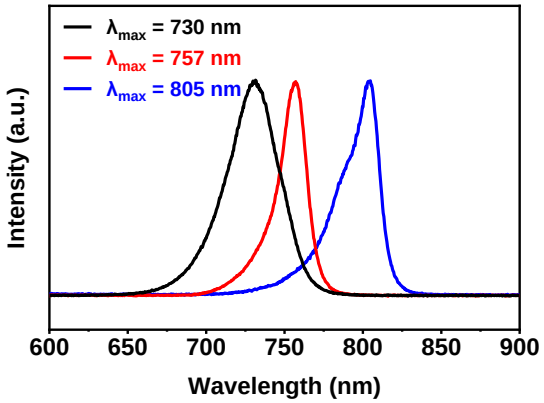

Figure S3. Emission spectra of the three NIR lights used in this study.

Table S1. Results of control experiments for the polymerization conducted using ZnPc particles [a]

Entry	[Brij 98] (mg mL^{-1})	[ZnPc] (ppm)	Conv. (%)[b]	$M_{n,th}$ (kg mol^{-1})[c]	M_n (kg mol^{-1})[d]	$Đ$[d]
1	0	4	14	-	Not run	Not run
2	10	4	58	29.1	25.0	1.03
3	10	0	<1	-	-	-

[a] Polymerization conditions: 300 µL, [DMA] = 30% w/v, [CTPA]/[DMA] = 1:500, [GOx] = 150 U mL^{-1}, [glucose] = 20 mM, NIR light (λ_{max} = 730 nm, I = 70 mW cm^{-2}). [b] Dtermined by ^{1}H NMR studies (D_2O). [c] $M_{n,th} = M_{CTPA} + 500 \times$ conversion% $\times M_{DMA}$. [d] M_n and dispersity data determined by MALLS-GPC.

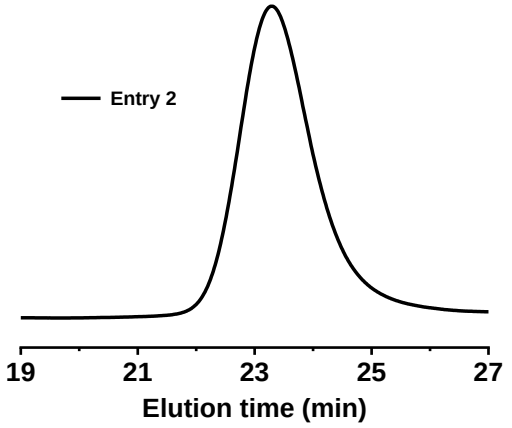

Figure S4. GPC trace recorded for the polymer presented in Table S1.

Table S2. Kinetic data for a DMA polymerization conducted at 70 mW cm^{-2} using ZnPc in the absence of Brij 98 [a]

Entry	Time (h)	Conv. (%)[b]	$M_{n,th}$ (kg mol^{-1})[c]	M_n (kg mol^{-1})[d]	$Đ$[d]
1	1	<1	-	-	-
2	2	<1	-	-	-
3	4	<1	-	-	-
4	6	<1	-	-	-
5	8	6	3.3	Not run	Not run
6	10	14	7.2	Not run	Not run

[a] Polymerization conditions: 300 µL, [DMA] = 30% w/v, [CTPA]/[DMA] = 1:500, [GOx] = 150 U mL^{-1}, [glucose] = 20 mM, [ZnPc] = 4 ppm, [Brij 98] = 0 mg mL^{-1}, NIR light (λ_{max} = 730 nm, I = 70 mW cm^{-2}). [b] Dtermined by ^{1}H NMR studies (D_2O). [c] $M_{n,th} = M_{CTPA} + 500 \times$ conversion% $\times M_{DMA}$. [d] M_n and dispersity data determined by MALLS-GPC.

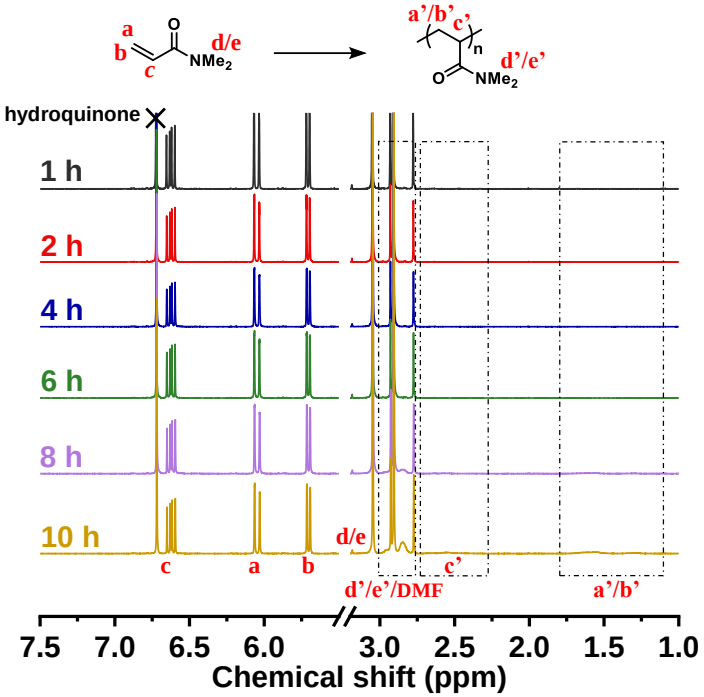

Figure S5. ^{1}H NMR spectra recorded in D_2O during the NIR-mediated DMA polymerization conducted at 70 mW cm^{-2} in the absence of Brij 98 (corresponding to Table S2).

Table S3. Kinetic data for a DMA polymerization conducted at 70 mW cm^{-2} using ZnPc at [Brij 98] = 5 mg mL^{-1} [a]

Entry	Time (h)	Conv. (%)[b]	$M_{n,th}$ (kg mol^{-1})[c]	M_n (kg mol^{-1})[d]	$Đ$[d]
1	1	<1	-	-	-
2	2	<1	-	-	-
3	4	16	8.2	Not run	Not run
4	6	28	14.2	12.5	1.05
5	8	38	19.1	17.2	1.04
6	10	45	22.6	21.9	1.05

[a] Polymerization conditions: 300 µL, [DMA] = 30% w/v, [CTPA]/[DMA] = 1:500, [GOx] = 150 U mL^{-1}, [glucose] = 20 mM, [ZnPc] = 4 ppm, [Brij 98] = 5 mg mL^{-1}, NIR light (λ_{max} = 730 nm, I = 70 mW cm^{-2}). [b] Dtermined by ^{1}H NMR studies (D_2O). [c] $M_{n,th} = M_{CTPA} + 500 \times$ conversion% $\times M_{DMA}$. [d] M_n and dispersity data determined by MALLS-GPC.

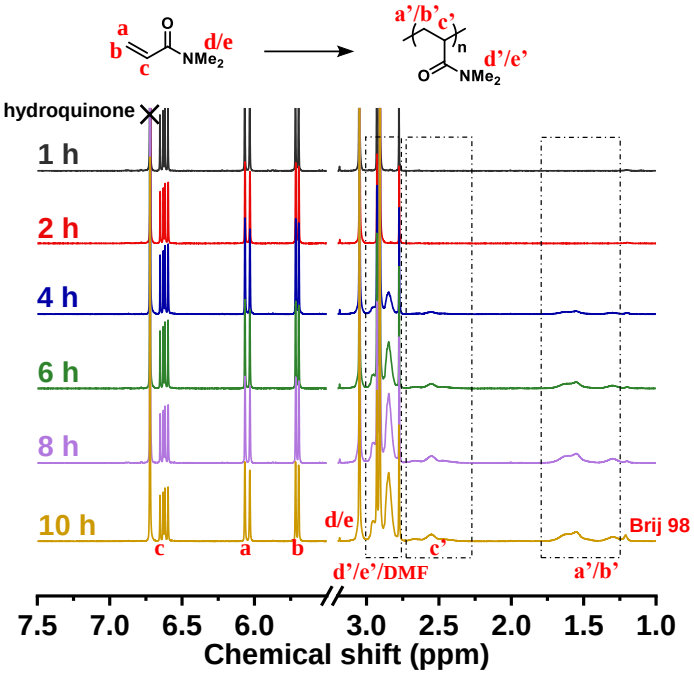

Figure S6. ^{1}H NMR spectra recorded in D_2O during the NIR-mediated DMA polymerization conducted at 70 mW cm^{-2}, [Brij 98] = 5 mg mL^{-1} (corresponding to Table S3).

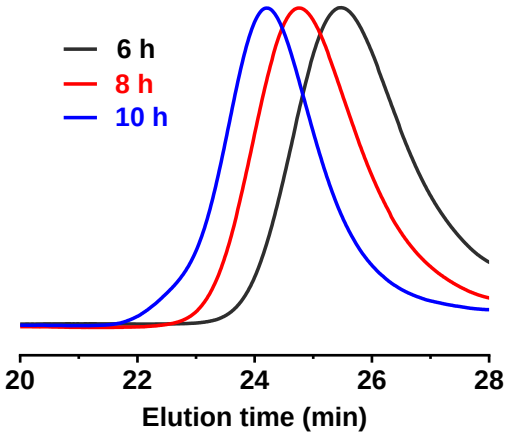

Figure S7. GPC traces recorded for the polymers obtained at various polymerization times (corresponding to Table S3).

Table S4. Kinetic data for a DMA polymerization conducted at 70 mW cm^{-2} using ZnPc at [Brij 98] = 10 mg mL^{-1} [a]

Entry	Time (h)	Conv. (%)[b]	$M_{n,th}$ (kg mol^{-1})[c]	M_n (kg mol^{-1})[d]	$Đ$[d]
1	1	<1	-	-	-
2	2	<1	-	-	-
3	4	19	9.7	Not run	Not run
4	6	34	17.2	18.8	1.13
5	8	43	21.6	19.5	1.03
6	10	47	23.6	23.6	1.08

[a] Polymerization conditions: 300 µL, [DMA] = 30% w/v, [CTPA]/[DMA] = 1:500, [GOx] = 150 U mL^{-1}, [glucose] = 20 mM, [ZnPc] = 4 ppm, [Brij 98] = 10 mg mL^{-1}, NIR light (λ_{max} = 730 nm, I = 70 mW cm^{-2}). [b] Dtermined by ^{1}H NMR studies (D_2O). [c] $M_{n,th} = M_{CTPA} + 500 \times$ conversion% $\times M_{DMA}$. [d] M_n and dispersity data determined by MALLS-GPC.

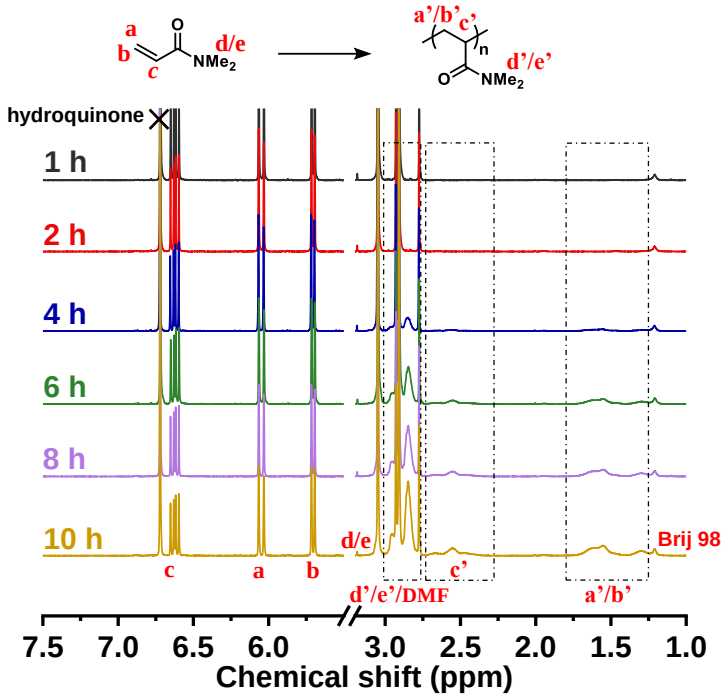

Figure S8. ^{1}H NMR spectra recorded in D_2O during the NIR-mediated DMA polymerization conducted at 70 mW cm^{-2}, [Brij 98] = 10 mg mL^{-1} (corresponding to Table S4).

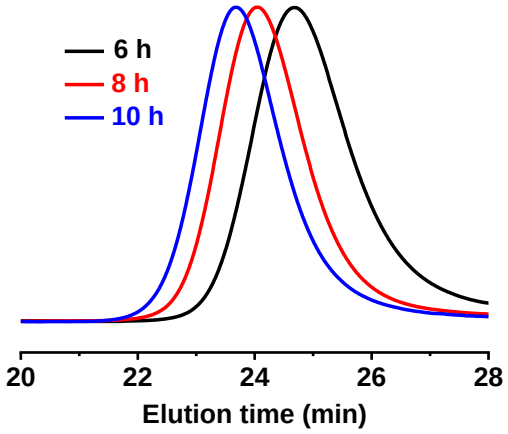

Figure S9. GPC traces recorded for the polymers obtained at various polymerization times (corresponding to Table S4).

Table S5. Kinetic data for a DMA polymerization conducted at 140 mW cm^{-2} using ZnPc at [Brij 98] = 10 mg mL^{-1} [a]

Entry	Time (h)	Conv. (%)[b]	$M_{n,th}$ (kg mol^{-1})[c]	M_n (kg mol^{-1})[d]	$Đ$[d]
1	1	<1	-	-	-
2	2	4	2.3	Not run	Not run
3	4	32	16.2	15.3	1.20
4	6	47	23.6	20.6	1.02
5	8	58	29.1	27.1	1.03
6	10	63	31.5	29.7	1.03

[a] Polymerization conditions: 300 µL, [DMA] = 30% w/v, [CTPA]/[DMA] = 1:500, [GOx] = 150 U mL^{-1}, [glucose] = 20 mM, [ZnPc] = 4 ppm, [Brij 98] = 10 mg mL^{-1}, NIR light (λ_{max} = 730 nm, I = 140 mW cm^{-2}). [b] Dtermined by ^{1}H NMR studies (D_2O). [c] $M_{n,th} = M_{CTPA} + 500 \times$ conversion% $\times M_{DMA}$. [d] M_n and dispersity data determined by MALLS-GPC.

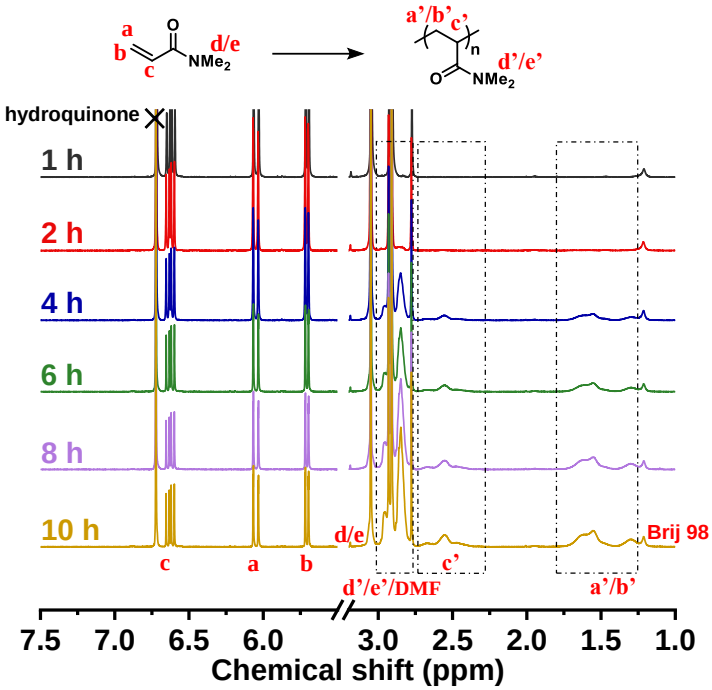

Figure S10. ^{1}H NMR spectra recorded in D_2O during the NIR-mediated DMA polymerization conducted at 140 mW cm^{-2}, [Brij 98] = 10 mg mL^{-1} (corresponding to Table S5).

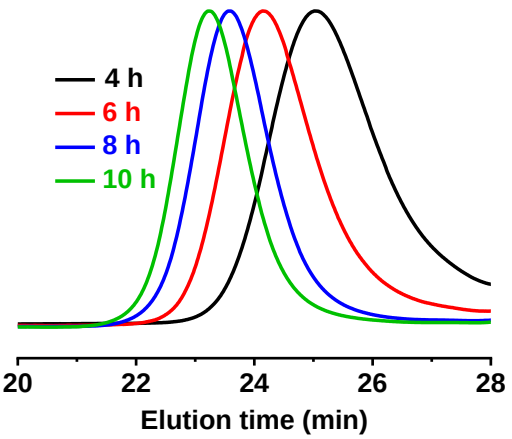

Figure S11. GPC traces recorded for polymers obtained at various polymerization times (corresponding to Table S5).

Table S6. Kinetic data for a DMA polymerization conducted at 140 mW cm^{-2} using ZnPc at [Brij 98] = 20 mg mL^{-1} [a]

Entry	Time (h)	Conv. (%)[b]	$M_{n,th}$ (kg mol^{-1})[c]	M_n (kg mol^{-1})[d]	$Đ$[d]
1	1	<1	-	-	-
2	2	7	3.8	-	-
3	4	34	17.2	15.6	1.04
4	6	49	24.6	21.6	1.03
5	8	58	29.1	27.9	1.05
6	10	64	32.0	31.7	1.03

[a] Polymerization conditions: 300 µL, [DMA] = 30% w/v, [CTPA]/[DMA] = 1:500, [GOx] = 150 U mL^{-1}, [glucose] = 20 mM, [ZnPc] = 4 ppm, [Brij 98] = 20 mg mL^{-1}, NIR light (λ_{max} = 730 nm, I = 140 mW cm^{-2}). [b] Dtermined by ^{1}H NMR studies (D_2O). [c] $M_{n,th} = M_{CTPA} + 500 \times$ conversion% $\times M_{DMA}$. [d] M_n and dispersity data determined by MALLS-GPC.

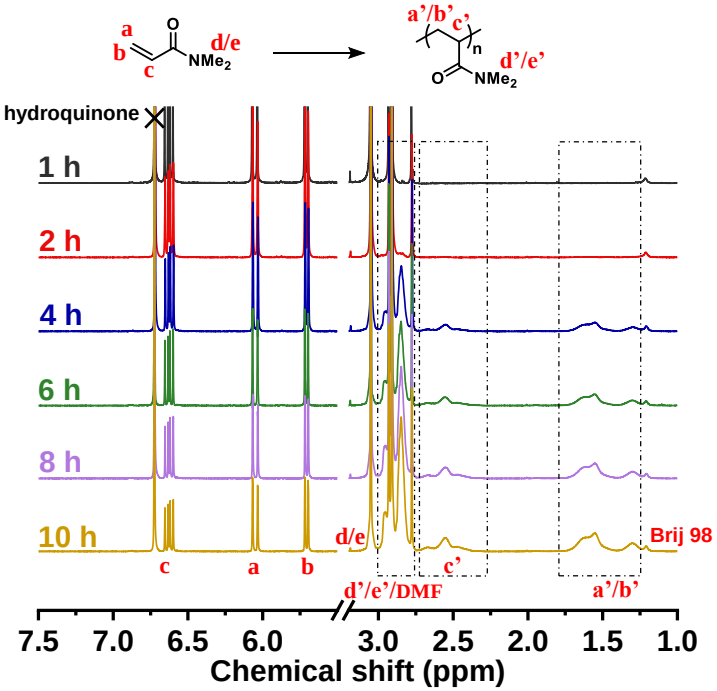

Figure S12. ^{1}H NMR spectra recorded in D_2O during the NIR-mediated DMA polymerization conducted at 140 mW cm^{-2}, [Brij 98] = 20 mg mL^{-1} (corresponding to Table S6).

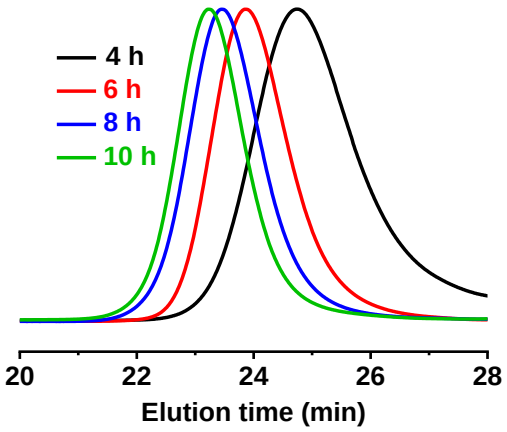

Figure S13. GPC traces recorded for the polymers obtained at various polymerization times (corresponding to Table S6).

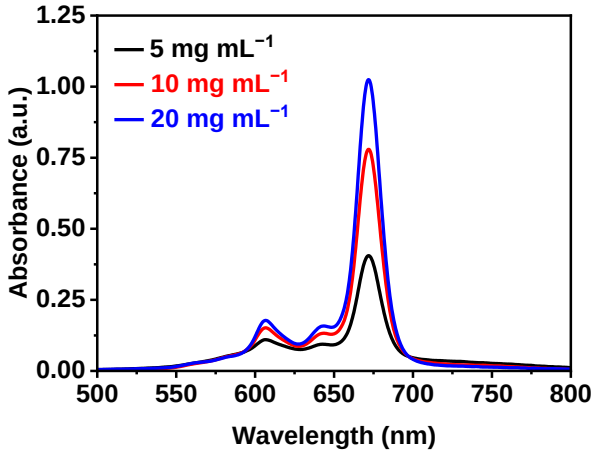

Figure S14. Visible absorption spectra of ZnPc in DMA phosphate buffer solution (30% w/v) containing different concertrations of Brij 98.

Table S7. Kinetic data for a DMA polymerization conducted in the absence of ZnPc at 140 mW cm^{-2}, [Brij 98] = 20 mg mL^{-1} [a]

Entry	Time (h)	Conv. (%)[b]	$M_{n,th}$ (kg mol^{-1})[c]	M_n (kg mol^{-1})[d]	$Đ$[d]
1	1	<1	-	-	-
2	2	<1	-	-	-
3	4	<1	-	-	-
4	6	<1	-	-	-
5	8	<1	-	-	-
6	10	<1	-	-	-

[a] Polymerization conditions: 300 µL, [DMA] = 30% w/v, [CTPA]/[DMA] = 1:500, [GOx] = 150 U mL^{-1}, [glucose] = 20 mM, [ZnPc] = 0 ppm, [Brij 98] = 20 mg mL^{-1}, NIR light (λ_{max} = 730 nm, I = 140 mW cm^{-2}). [b] Dtermined by ^{1}H NMR studies (D_2O). [c] $M_{n,th} = M_{CTPA} + 500 \times$ conversion% $\times M_{DMA}$. [d] M_n and dispersity data determined by MALLS-GPC.

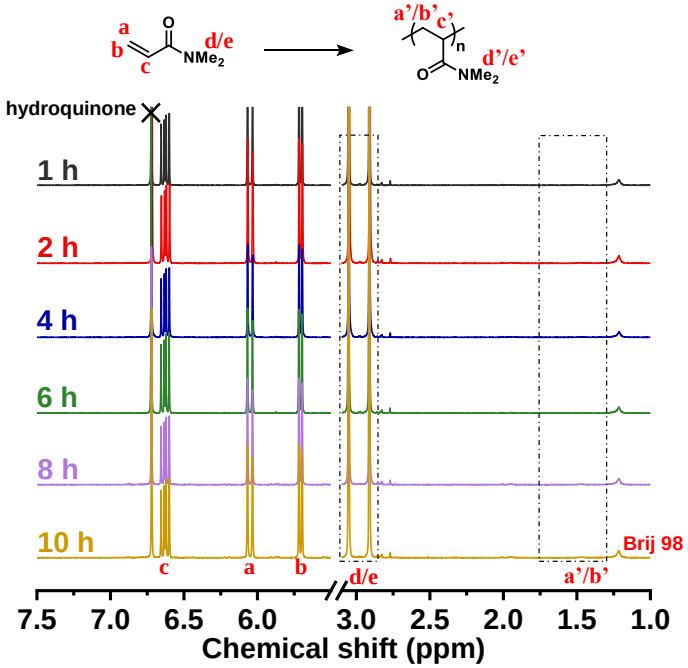

Figure S15. ^{1}H NMR spectra recorded in D_2O during the NIR-mediated DMA polymerization conducted at [ZnPc] = 0 ppm, 140 mW cm^{-2}, [Brij 98] = 20 mg mL^{-1} (corresponding to Table S7).

Table S8. Summary of the homopolymers synthesized via high-throughput RAFT polymerizations[a]

Entry	Monomer	Target DP	Conv. (%)[d]	$M_{n,\,th}$ (kg mol^{-1})[e]	M_n (kg mol^{-1})[f]	$Đ$[f]
1[b]	DMA	1,000	53	52.8	50.0	1.05
2[b]	DMA	2,000	58	115	90.4	1.06
3[b]	DMA	4,000	60	238	230	1.18
4[b]	DMA	8,000	60	476	429	1.24
5[b]	DMA	10,000	60	595	594	1.39
6[b]	DMA	20,000	57	1130	918	1.39
7[c]	NAM	500	78	55.4	49.1	1.03
8[c]	NAM	1,000	74	105	128	1.08
9[c]	NAM	2,000	72	204	194	1.13
10[c]	PEGA	50	61	14.9	12.2	1.13
11[c]	PEGA	100	71	34.4	33.1	1.23
12[c]	PEGA	200	70	67.5	60.1	1.21
13[c]	PEGMA	50	89	22.6	17.4	1.16
14[c]	PEGMA	100	66	33.3	42.0	1.25

[a] Polymerization conditions: 300 µL, [DMA] = 30% w/v, CTPA as the CTA, [GOx] = 150 U mL^{-1}, [glucose] = 20 mM, [ZnPc] = 4 ppm, [Brij 98] = 10 mg mL^{-1}, NIR light (λ_{max} = 730 nm). [b] I = 70 mW cm^{-2}. [c] I = 14mW cm^{-2}. [d] Dtermined by ^{1}H NMR studies (D_2O). [e] $M_{n,th} = M_{CTPA}$ + target DP × conversion% × M_{DMA}. [f] M_n and dispersity data determined by MALLS-GPC.

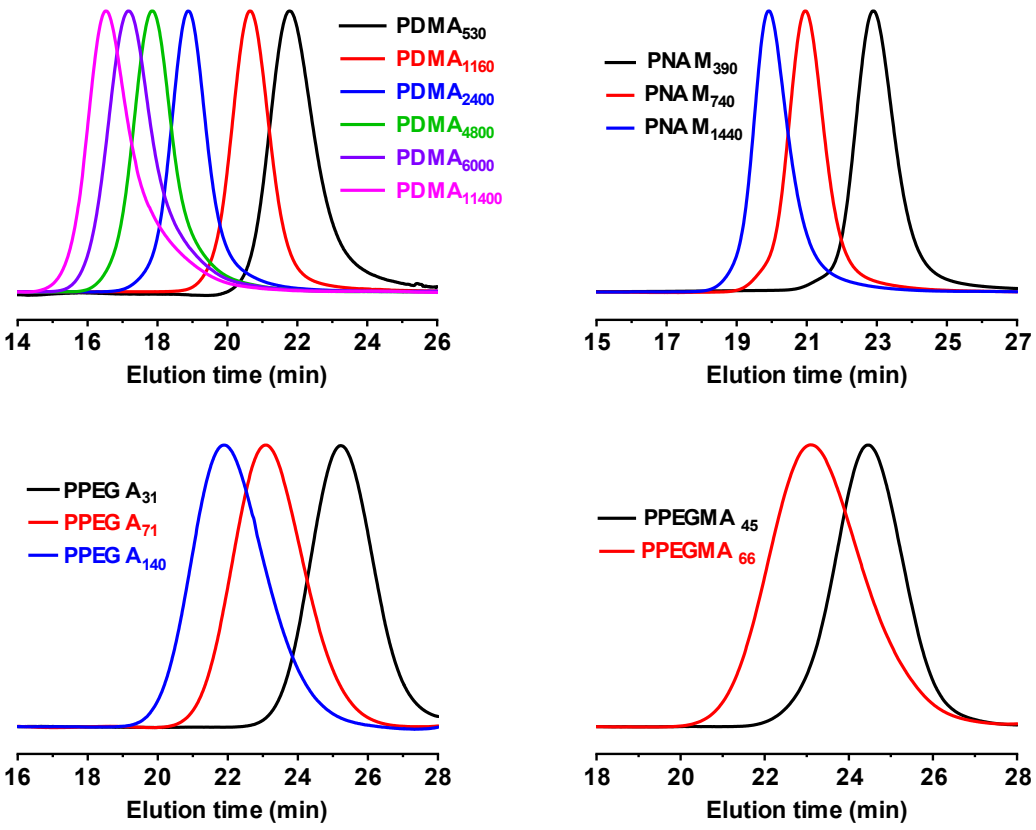

Figure S16. GPC traces recorded for the polymers presented in Table S8.

Table S9. Kinetic data for a DMA polymerization targeting DP = 15,000 [a]

Entry	Time (h)	Conv. (%)[b]	$M_{n,th}$ (kg mol^{-1})[c]	M_n (kg mol^{-1})[d]	$Đ$[d]
1	2	<1	-	-	-
2	4	15	223	197	1.30
3	7	33	491	397	1.33
4	10	40	595	530	1.45
5	12	54	803	609	1.44
6	14	63	937	900	1.39

[a] Polymerization conditions: 300 µL, [DMA] = 30% w/v, [CTPA]/[DMA] = 1:15,000, [GOx] = 150 U mL^{-1}, [glucose] = 20 mM, [ZnPc] = 4 ppm, [Brij 98] = 10 mg mL^{-1}, NIR light (λ_{max} = 730 nm, I = 70 mW cm^{-2}). [b] Dtermined by ^{1}H NMR studies (D_2O). [c] $M_{n,th} = M_{CTPA} + 15{,}000 \times$ conversion% $\times M_{DMA}$. [d] M_n and dispersity data determined by MALLS-GPC.

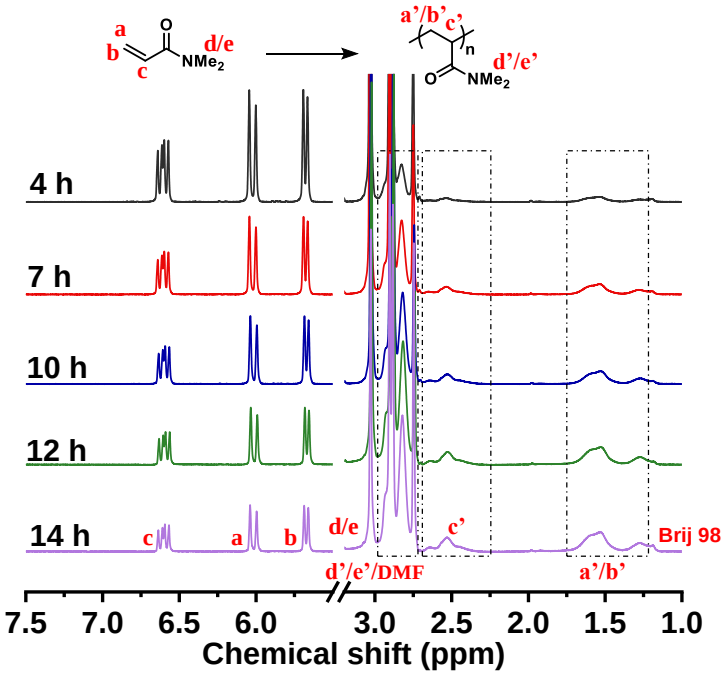

Figure S17. ^{1}H NMR spectra recorded in D_2O during the NIR-mediated DMA polymerization conducted at targeting DP = 15,000 (corresponding to Table S9).

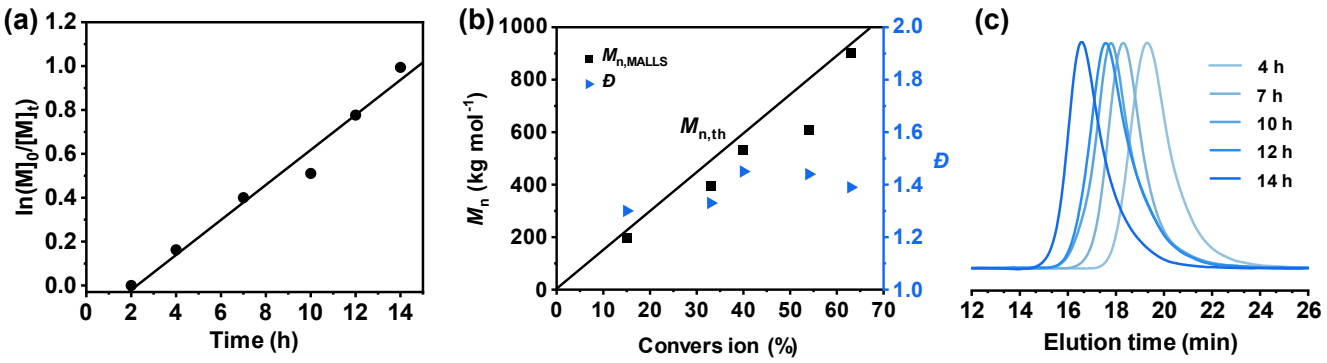

Figure S18. Polymerization kinetic data for the synthesis of UHMW PDMA (corresponding to Table S9). (a) ln([M]$_0$/[M]$_t$) *vs* time plot. (b) Evolution of M_n and dispersity *vs* conversion. (c) GPC traces recorded for the polymers obtained at various times.

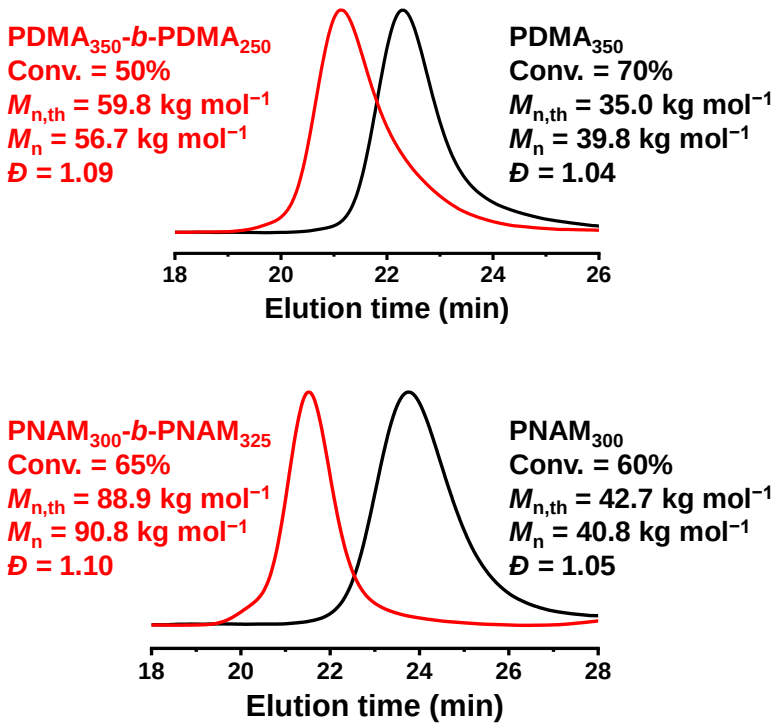

Figure S19. Results for block copolymers synthesis. First block: 200 µL, 30% w/v, [CTPA]/[monomer] = 1:500, [ZnPc] = 4 ppm, [Brij 98] = 10 mg mL^{-1}, [GOx] = 150 U mL^{-1}, [glucose] = 20 mM, phosphate buffer (0.2 M, pH 5.7), 12 h, NIR light (λ_{max} = 730 nm; I = 140 mW cm^{-2}). Second block: 300 µL, [Macro-CTA]/[monomer] = 1:500, [ZnPc] = 4 ppm, [Brij 98] = 10 mg mL^{-1}, [GOx] = 150 U mL^{-1}, [glucose] = 20 mM, 12 h, NIR light (λ_{max} = 730 nm; I = 140 mW cm^{-2}).

Table S10. Polymerization results of "on/off" modulation [a]

Entry	Time (h)	Conv. (%)[b]	$M_{n,th}$ (kg mol^{-1})[c]	M_n (kg mol^{-1})[d]	$Đ$[d]
1	1	0	-	-	-
2	2	6	3.3	Not run	Not run
3	3	15	7.7	Not run	Not run
4	6	15	7.7	Not run	Not run
5	7	34	17.2	15.7	1.03
6	10	34	17.2	15.8	1.03
7	12	47	23.6	21.5	1.02

[a] Polymerization conditions: 300 µL, [DMA] = 30% w/v, [CTPA]/[DMA] = 1:500, [GOx] = 150 U mL^{-1}, [glucose] = 20 mM, [ZnPc] = 4 ppm, [Brij 98] = 10 mg mL^{-1}, NIR light (λ_{max} = 730 nm, I = 140 mW cm^{-2}). [b] Dtermined by ^{1}H NMR studies (D_2O). [c] $M_{n,th} = M_{CTPA} + 500 \times$ conversion% $\times M_{DMA}$. [d] M_n and dispersity data determined by MALLS-GPC.

2.3 RAFT polymerization using ZnTtBNc particles

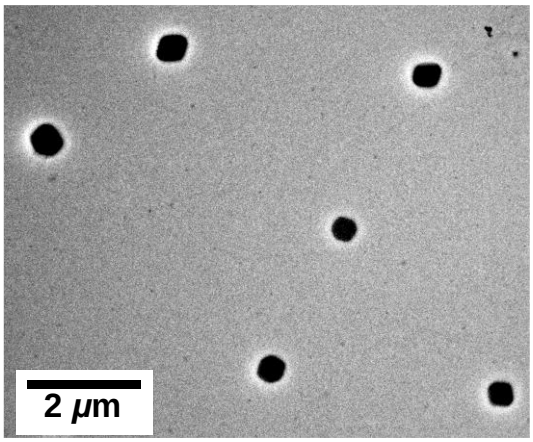

Figure S20. TEM micrograph recorded for Brij 98-stabilized ZnTtBNc particles.

Table S11. Results of control experiments for the polymerization conducted using ZnTtBNc particles [a]

Entry	[GOx] (U mL^{-1})	[glucose] (mM)	[Brij 98] (mg mL^{-1})	Conv. (%)[d]
1[b]	0	0	0	<5
2[b]	0	0	10	17
3[c]	150	20	0	<5
4[c]	150	20	10	50

[a] Polymerization conditions: 2 mL, [DMA] = 30% w/v, [CTPA]/[DMA] = 1:500, [ZnTtBNc] = 4 ppm, NIR light (λ_{max} = 757 nm, I = 70 mW cm^{-2}). [b] with Ar bubbling for deoxygenation. [c] no prior deoxygenation. [d] Dtermined by ^{1}H NMR studies (D_2O).

Table S12. Kinetic data for a DMA polymerization conducted under conditions: λ_{max} = 757 nm, 70 mW cm^{-2}, [ZnTtBNc] = 4 ppm, [Brij 98] = 10 mg mL^{-1} [a]

Entry	Time (h)	Conv. (%)[b]	$M_{n,th}$ (kg mol^{-1})[c]	M_n (kg mol^{-1})[d]	$Đ$[d]
1	1	<1	-	-	-
2	2	<1	-	-	-
3	3	12	6.3	Not run	Not run
4	4	14	7.2	Not run	Not run
5	6	26	13.2	12.1	1.14
6	8	29	14.7	15.3	1.10
7	12	47	23.6	21.9	1.06

[a] Polymerization conditions: 300 µL, [DMA] = 30% w/v, [CTPA]/[DMA] = 1:500, [GOx] = 150 U mL^{-1}, [glucose] = 20 mM, [ZnTtBNc] = 4 ppm, [Brij 98] = 10 mg mL^{-1}, NIR light (λ_{max} = 757 nm, I = 70 mW cm^{-2}). [b] Dtermined by ^{1}H NMR studies (D_2O). [c] $M_{n,th} = M_{CTPA} + 500 \times$ conversion% $\times M_{DMA}$. [d] M_n and dispersity data determined by MALLS-GPC.

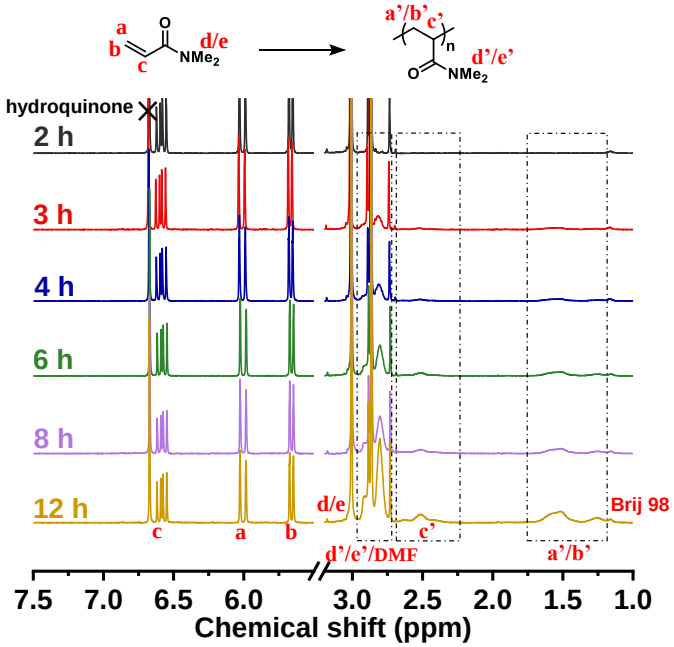

Figure S21. ^{1}H NMR spectra recorded in D_2O during the NIR-mediated DMA polymerization conducted under conditions: λ_{max} = 757 nm, 70 mW cm^{-2}, [ZnTtBNc] = 4 ppm, [Brij 98] = 10 mg mL^{-1} (corresponding to Table S12).

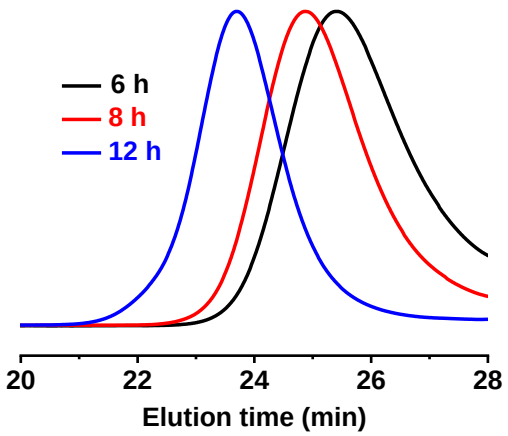

Figure S22. GPC traces recorded for the polymers obtained at various polymerization times (corresponding to Table S12).

Table S13. Kinetic data for a DMA polymerization conducted under conditions: λ_{max} = 805 nm, 70 mW cm^{-2}, [ZnTtBNc] = 4 ppm, [Brij 98] = 10 mg mL^{-1} [a]

Entry	Time (h)	Conv. (%)[b]	$M_{n,th}$ (kg mol^{-1})[c]	M_n (kg mol^{-1})[d]	$Đ$[d]
1	1	<1	-	-	-
2	2	<1	-	-	-
3	3	<1	-	-	-
4	4	<1	-	-	-
5	6	3	1.8	Not run	Not run
6	8	21	10.7	Not run	Not run
7	10	31	15.7	16.1	1.06

[a] Polymerization conditions: 300 µL, [DMA] = 30% w/v, [CTPA]/[DMA] = 1:500, [GOx] = 150 U mL^{-1}, [glucose] = 20 mM, [ZnTtBNc] = 4 ppm, [Brij 98] = 10 mg mL^{-1}, NIR light (λ_{max} = 805 nm, I = 70 mW cm^{-2}). [b] Dtermined by ^{1}H NMR studies (D_2O). [c] $M_{n,th} = M_{CTPA} + 500 \times$ conversion% $\times M_{DMA}$. [d] M_n and dispersity data determined by MALLS-GPC.

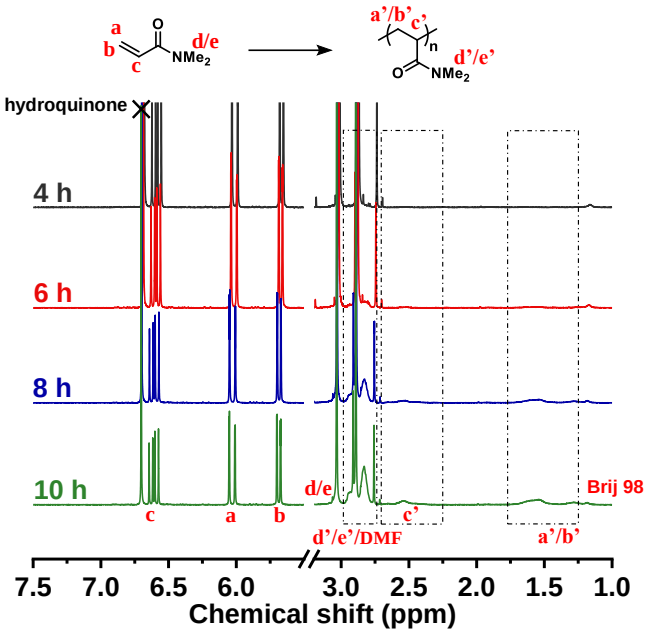

Figure S23. ^{1}H NMR spectra recorded in D_2O during the NIR-mediated DMA polymerization conducted under conditions: λ_{max} = 805 nm, 70 mW cm^{-2}, [ZnTtBNc] = 4 ppm, [Brij 98] = 10 mg mL^{-1} (corresponding to Table S13).

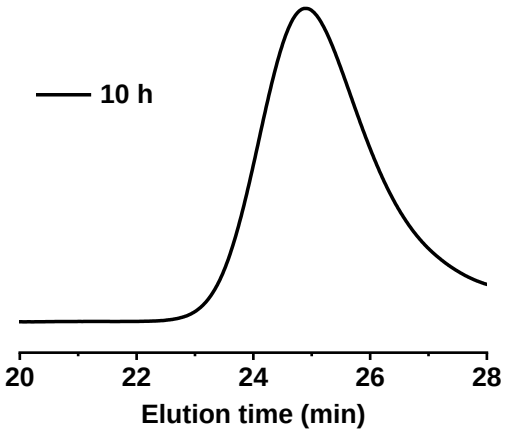

Figure S24. GPC trace recorded for the polymer obtained at the 10th hour (corresponding to Table S13).

Table S14. Kinetic data for a DMA polymerization conducted under conditions: λ_{max} = 805 nm, 200 mW cm^{-2}, [ZnTtBNc] = 4 ppm, [Brij 98] = 10 mg mL^{-1} [a]

Entry	Time (h)	Conv. (%)[b]	$M_{n,th}$ (kg mol^{-1})[c]	M_n (kg mol^{-1})[d]	$Đ$[d]
1	1	<1	-	-	-
2	2	<1	-	-	-
3	3	5	-	-	-
4	4	9	-	-	-
5	6	17	8.7	Not run	Not run
6	8	29	14.7	13.3	1.10
7	10	43	21.6	20.0	1.05

[a] Polymerization conditions: 300 µL, [DMA] = 30% w/v, [CTPA]/[DMA] = 1:500, [GOx] = 150 U mL^{-1}, [glucose] = 20 mM, [ZnTtBNc] = 4 ppm, [Brij 98] = 10 mg mL^{-1}, NIR light (λ_{max} = 805 nm, I = 200 mW cm^{-2}). [b] Dtermined by ^{1}H NMR studies (D_2O). [c] $M_{n,th} = M_{CTPA} + 500 \times$ conversion% $\times M_{DMA}$. [d] M_n and dispersity data determined by MALLS-GPC.

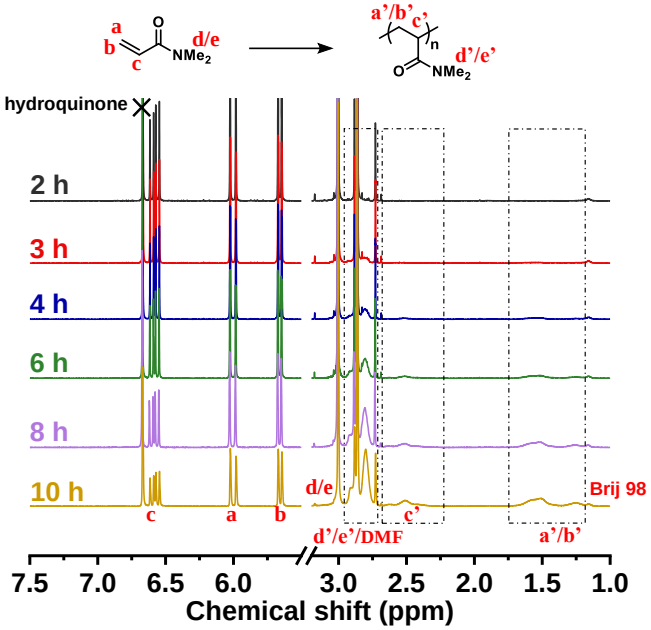

Figure S25. ^{1}H NMR spectra recorded in D_2O during the NIR-mediated DMA polymerization conducted under conditions: λ_{max} = 805 nm, 200 mW cm^{-2}, [ZnTtBNc] = 4 ppm, [Brij 98] = 10 mg mL^{-1} (corresponding to Table S14).

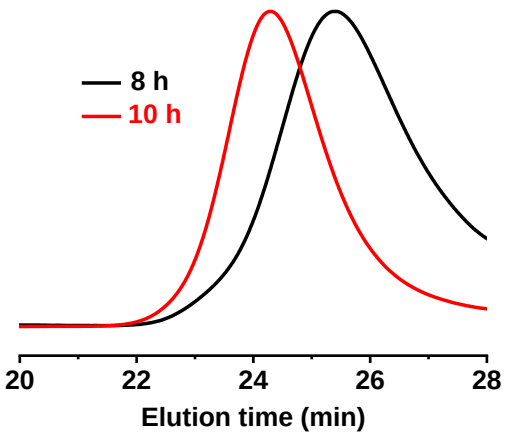

Figure S26. GPC traces recorded for polymers obtained at various polymerization times (corresponding to Table S14).

Table S15. Kinetic data for a DMA polymerization conducted under conditions: λ_{max} = 805 nm, 200 mW cm^{-2}, [ZnTtBNc] = 10 ppm, [Brij 98] = 20 mg mL^{-1} [a]

Entry	Time (h)	Conv. (%)[b]	$M_{n,th}$ (kg mol^{-1})[c]	M_n (kg mol^{-1})[d]	$Đ$[d]
1	1	<1	-	-	-
2	2	<1	-	-	-
3	3	11	-	-	-
4	4	19	-	-	-
5	6	31	15.7	14.9	1.05
6	8	39	19.6	18.6	1.05
7	10	49	24.6	24.1	1.03

[a] Polymerization conditions: 300 µL, [DMA] = 30% w/v, [CTPA]/[DMA] = 1:500, [GOx] = 150 U mL^{-1}, [glucose] = 20 mM, [ZnTtBNc] = 10 ppm, [Brij 98] = 20 mg mL^{-1}, NIR light (λ_{max} = 805 nm, I = 200 mW cm^{-2}). [b] Dtermined by ^{1}H NMR studies (D_2O). [c] $M_{n,th} = M_{CTPA} + 500 \times \text{conversion\%} \times M_{DMA}$. [d] M_n and dispersity data determined by MALLS-GPC.

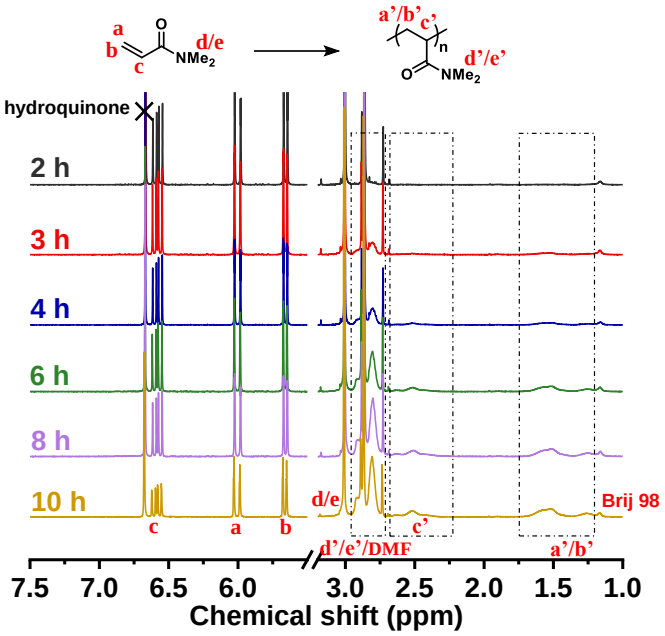

Figure S27. ^{1}H NMR spectra recorded in D_2O during the NIR-mediated DMA polymerization conducted under conditions: λ_{max} = 805 nm, 200 mW cm^{-2}, [ZnTtBNc] = 10 ppm, [Brij 98] = 20 mg mL^{-1} (corresponding to Table S15).

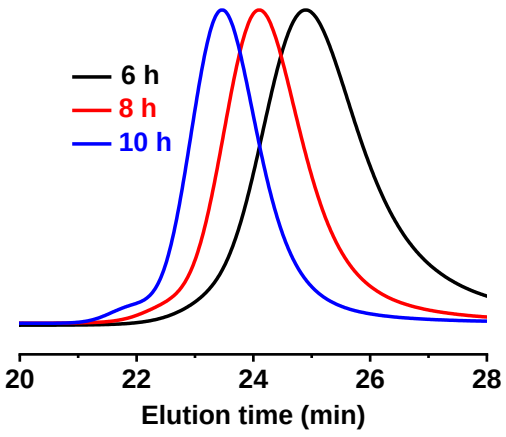

Figure S28. GPC traces recorded for the polymers obtained at various polymerization times (corresponding to Table S15).

Table S16. Results for the polymerization conducted using ZnTtBNc particles in the presence or absence of barriers [a]

Entry	Light intensity (mW cm^{-2})	barrier	Conv. (%)[b]	$M_{n,\,th}$ (kg mol^{-1})[c]	M_n (kg mol^{-1})[d]	$Đ$[d]
1	200	-	65	1,290	865	1.29
2	70	-	66	1,310	722	1.21
3	200	5 mm porcine skin	65	1,290	737	1.19
4	70	5 mm porcine skin	58	1,150	1,020	1.19

[a] Polymerization conditions: 2 mL vials with 2 mL solution, [DMA] = 30% w/v, [CTPA]/[DMA] = 1:20,000, [GOx] = 150 U mL^{-1}, [glucose] = 3 mM, [ZnTtBNc] = 4 ppm, [Brij 98] = 10 mg mL^{-1}, NIR light (λ_{max} = 805 nm). [b] Dtermined by ^{1}H NMR studies (D_2O). [c] $M_{n,th} = M_{CTPA}$ + 20,000 × conversion% × M_{DMA}. [d] M_n and dispersity data determined by MALLS-GPC.

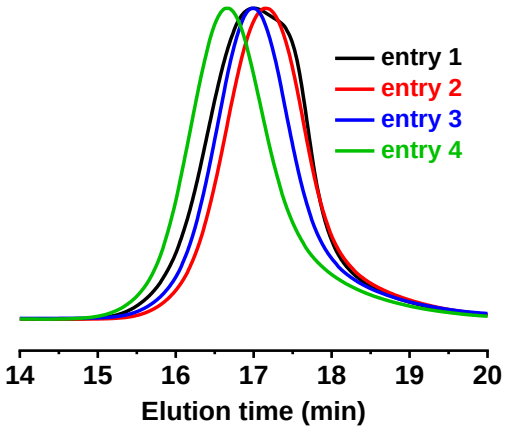

Figure S29. GPC traces recorded for the four homopolymers presented in Table S16.

Table S17. Polymerization conducted using ZnTtBNc particles without barrier at 25.8 mW cm^{-2} [a]

Entry	Conv. (%)[b]	$M_{n,\,th}$ (kg mol^{-1})[c]	M_n (kg mol^{-1})[d]	$Đ$[d]
1	60	1190	1050	1.14

[a] Polymerization conditions: 2 mL vial with 2 mL solution, [CTPA]/[DMA] = 1:20,000, 30% w/v, [ZnTtBNc] = 4 ppm relative to monomer, [Brij 98] = 10 mg mL^{-1}, [GOx] = 150 U mL^{-1}, [glucose] = 3 mM, phosphate buffer (0.2 M, pH 5.7), 500 rpm, 20 h, NIR light (λ_{max} = 805 nm, 25.8 mW cm^{-2}). [b] Dtermined by ^{1}H NMR studies (D_2O). [c] $M_{n,th} = M_{CTPA}$ + 20,000 × conversion% × M_{DMA}. [d] M_n and dispersity data determined by MALLS-GPC.