Electronic Supporting Information for

A reusable visible light initiation system for radical polymerizations in water

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1. Materials

N,N-dimethylacrylamide (DMA, TCI, >99%), 2-hydroxyethyl acrylate (2-HEA, TCI, >95%), *N*-isopropylacrylamide (NIPAm, TCI, >98%), *N,N*-diethylacrylamide (DEA, TCI, >98%), and 4-acryloylmorpholine (AMP, TCI, >98%) were purified by passing through a basic alumina (Al_2O_3) column to remove inhibitors before use. *N*-vinylpyrrolidone (*N*VP, Acros, 99%) and acrylic acid (AA, Acros, 99.5%) were purified by vacuum distillation to remove inhibitors prior to storage. Acrylamide (Am, Alfa, 99+%), 4-nitrophenylacetylene (4-NA, $C_8H_5NO_2$, TCI, >98%, Product No. E1223), diphenyliodonium chloride (Ph_2ICl, TCI, >98%), 4-((((2-carboxyethyl)thio)carbonothioyl)thio)-4-cyanopentanoic acid (CETCPA, $C_9H_{13}NO_4S_3$, Angene, 98%) RAFT agent, and deuterium oxide (D_2O, Acros, 99.5%) were used as received. Milli-Q water (18.2 MΩ cm) was used for all aqueous solutions in the experiments.

2. Characterization

^{1}H NMR spectra of the polymers were recorded with a Bruker 400 MHz spectrometer. 14 pieces of 8 W 420 nm mercury lamps from Panchum PR-2000(M) were used in the photocatalytic experiments. The synthesized polymer was characterized by a GPC equipped with three Waters columns (Styragel® HR 2 DMF, Styragel® HR 4 DMF, and Styragel® HR 5 DMF) using DMF-LiBr (0.1 M) as the eluent at 80 ºC with a flow rate of 1 mL×min^{-1}. The calibration was based on linear poly(methyl methacrylate) (PMMA) with molecular weights of 1.8×10^3 – 6.7×10^5 g×mol^{-1}. The number-averaged molecular weight (M_n), weight-averaged molecular weight (M_w), and $Đ$ of the polymer were obtained using a DIONEX Chromeleon software. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry

was conducted on a Bruker autoflex speed spectrometer equipped with a 355 nm smartbeam™-II laser. 1.0 μL of α-cyano-4-hydroxycinnamic acid (CHCA) matrix solution (10 mg×mL^{-1} in 50% acetonitrile + 0.1% trifluoroacetic acid) was first deposited on a MALDI plate and air-dried. Aliquots of a polymer solution (1 mg×mL^{-1} in 50% methanol) were then deposited onto the matrix spot for characterization. The mass spectra were analyzed using flexControl (version 3.4) and flexAanlysis (version 3.4) software. Fluorescence spectra were measured using a Hitachi F-2700 fluorescence spectrometer to investigate the fluorescence quenching behavior. The excitation wavelength was set at 285 nm, and the emission spectra were collected over 500–600 nm with a scan speed of 300 nm min^{-1}. The slit widths for excitation and emission were 5.0 nm and 20.0 nm, respectively. The PMT voltage was 250 V, and the response time was 0.04 s. Centrifugation experiments were performed using a Hettich UNIVERSAL 320 R centrifuge. Samples were centrifuged at 9000 rpm for 10 min at 4 °C to separate phases based on density. The supernatant was removed and the precipitated solids were collected for subsequent analysis.

3. General procedure for photopolymerization of *N,N*-dimethylacrylamide

Deionized water was first purged with nitrogen for approximately 30 min to remove dissolved oxygen. *N,N*-dimethylacrylamide (DMA, 1.66 mL) and deionized water (6 mL) were introduced into a Schlenk flask, thoroughly deaerated by four freeze–pump–thaw cycles, and backfilled with nitrogen. Separately, 4-nitrophenylacetylene (4-NA, 8 mg) and diphenyliodonium chloride (Ph_2ICl, 24 mg) were weighed into a round-bottom Schlenk flask, followed by four vacuum/nitrogen cycles to remove residual oxygen. Under a continuous nitrogen atmosphere, the deoxygenated liquid mixture was quickly transferred from the pointed Schlenk flask into the round-bottom flask containing the solid components. The reaction mixture was

stirred at ambient temperature and irradiated with visible light from fourteen 8 W mercury lamps (λ = 420 nm) for typically 150 min. After irradiation, the monomer conversion was determined by ^{1}H NMR spectroscopy. A small aliquot of the reaction mixture was diluted with D_2O for NMR analysis, while a portion of the isolated polymer was dried for molecular weight determination using gel permeation chromatography (GPC) or used in subsequent recycling experiments.

4. General procedure for fluorescence quenching experiment

4-Nitrophenylacetylene (4-NA) was employed as the fluorescent probe at a fixed concentration of 1.0×10^{-5} M, dissolved in oxygen-free acetonitrile (ACN). Different concentrations of quenchers (DMA, AMP and DEA) were added to the solution, and the fluorescence emission spectra were recorded under excitation at 285 nm (emission range: 500–600 nm).

5. Supplementary figures

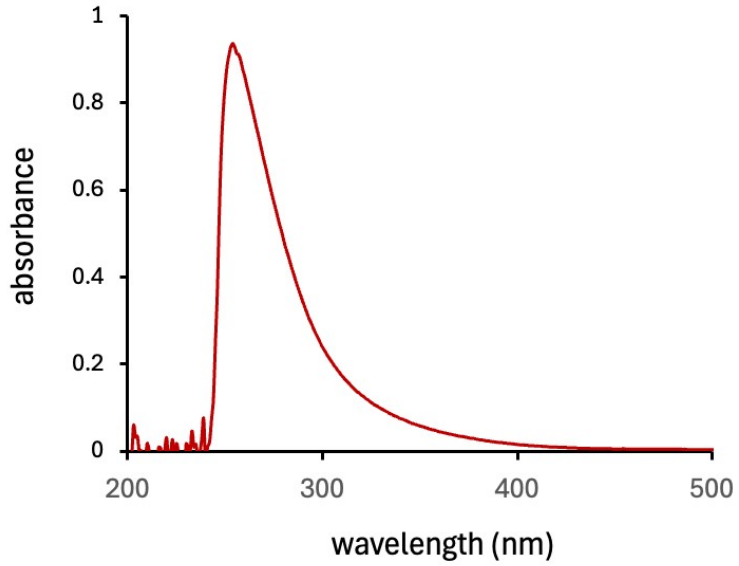

Figure S1. UV-vis spectrum of the 4-NA in 2.11M aqueous DMA.

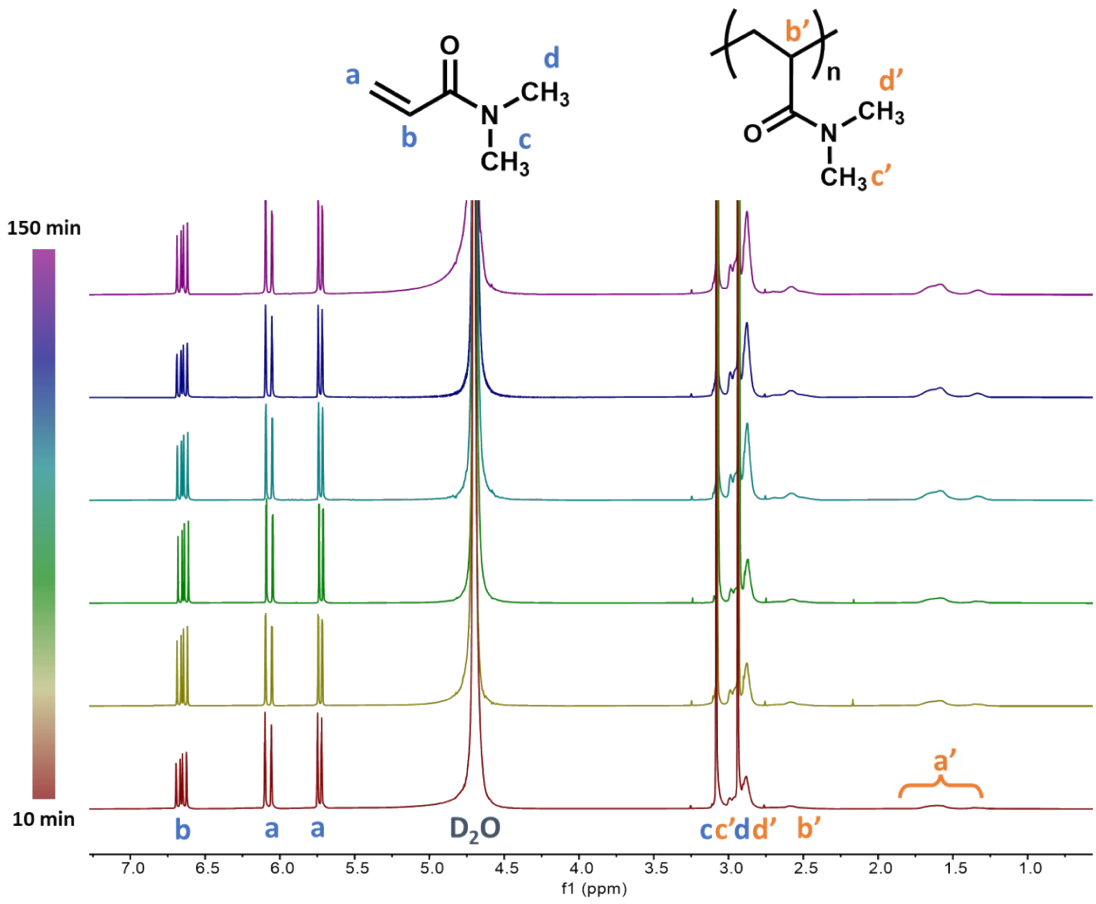

Figure S2. ^{1}H NMR spectra of DMA polymerization, which is carried out in deionized water using 2.11 M DMA and 0.5 wt% 4-NA, with the addition of 10 mM Ph_2ICl as a co-catalyst under 420 nm irradiation.

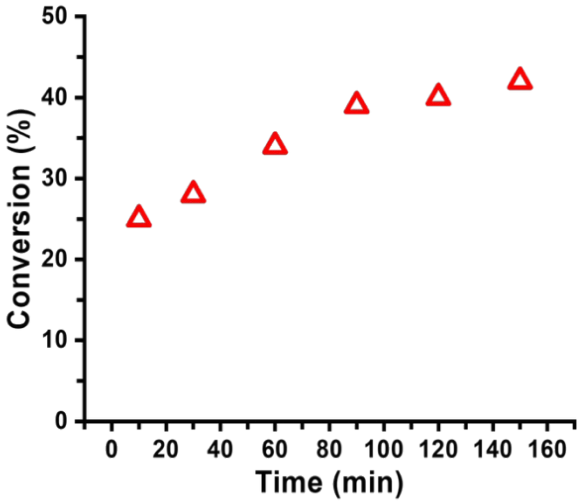

Figure S3. The evolution of monomer conversion according to reaction time. The reaction was conducted in deionized water using 2.11 M DMA and 0.5 wt% 4-NA, with the addition of 10 mM Ph_2ICl as a co-catalyst under 420 nm irradiation.

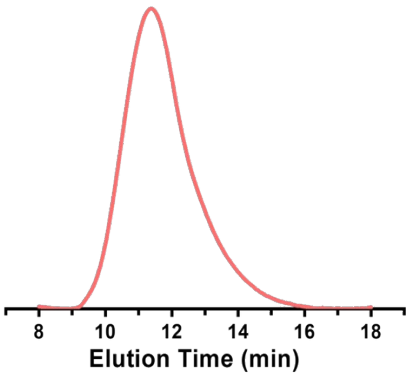

Figure S4. GPC traces of PDMA after a 150 minutes reaction. The reaction was conducted in deionized water using 2.11 M DMA and 0.5 wt% 4-NA, with the addition of 10 mM Ph_2ICl as a co-catalyst under 420 nm irradiation.

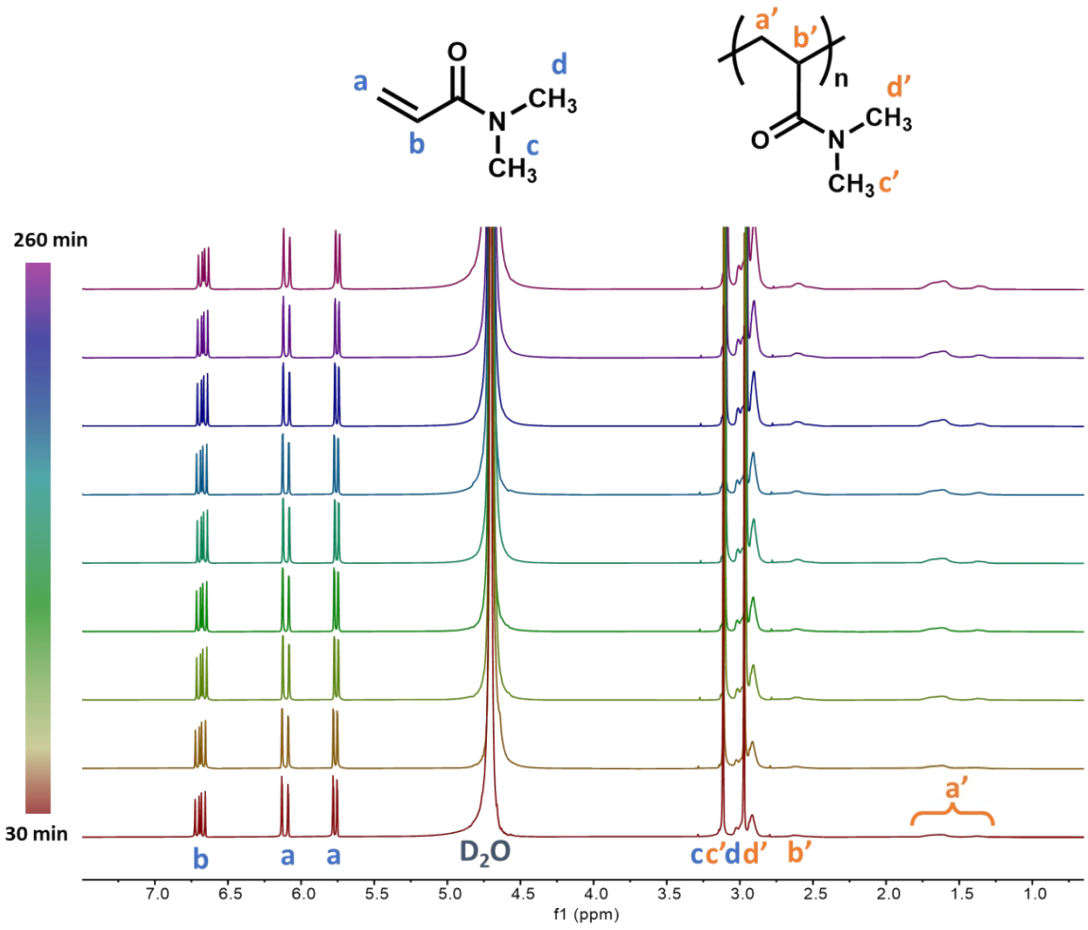

Figure S5. ^{1}H NMR spectra of DMA polymerization for the Intermittent light on/off experiment.

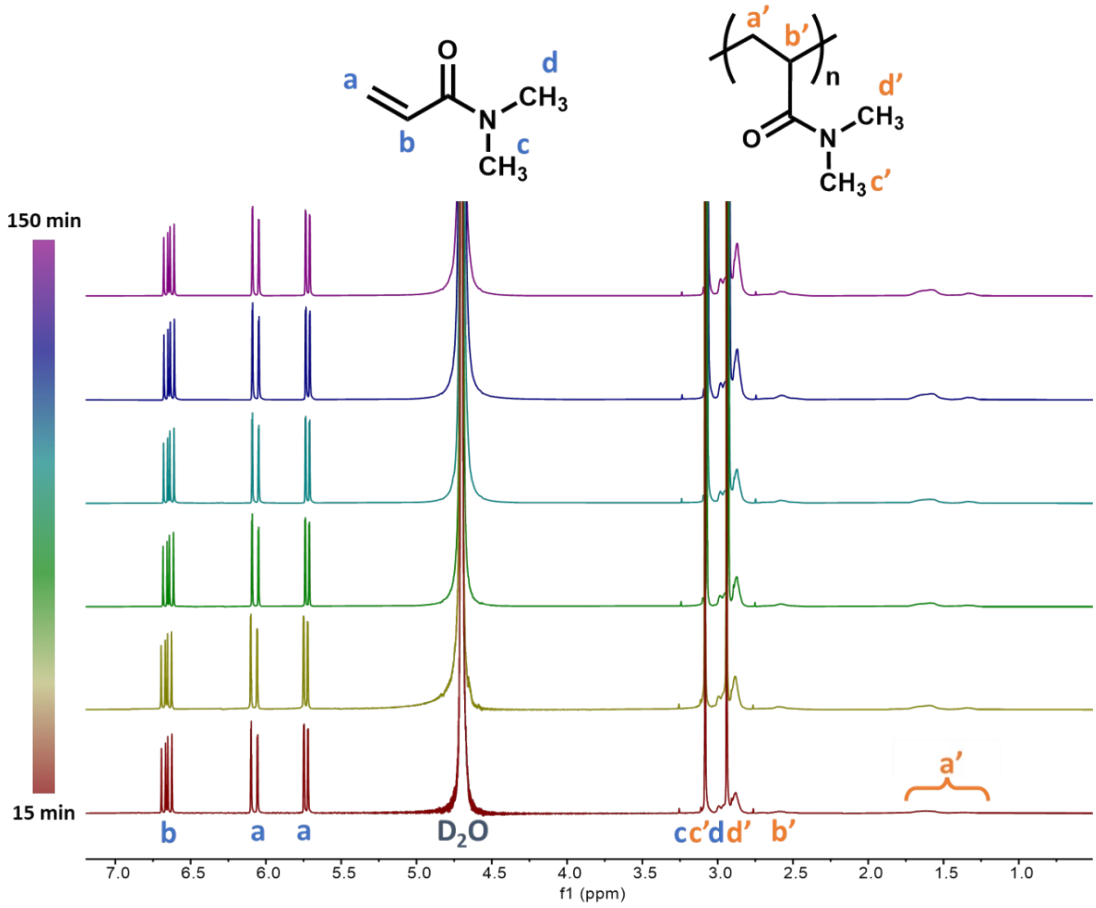

Figure S6. ^{1}H NMR spectra of DMA polymerization, which is carried out in deionized water using 2.11 M DMA and 0.5 wt% 4-NA under 420 nm irradiation.

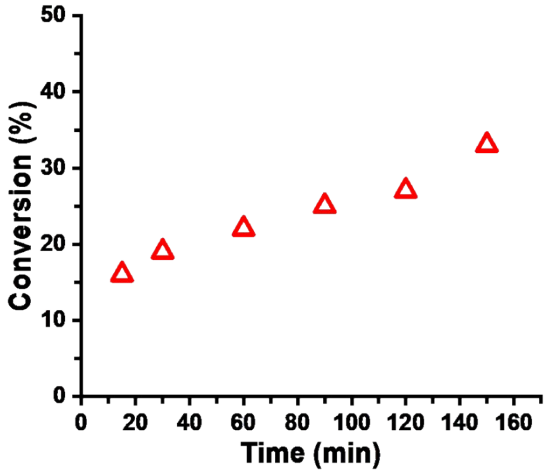

Figure S7. The evolution of monomer conversion according to reaction time. The reaction was conducted in deionized water using 2.11 M DMA and 0.5 wt% 4-NA under 420 nm irradiation.

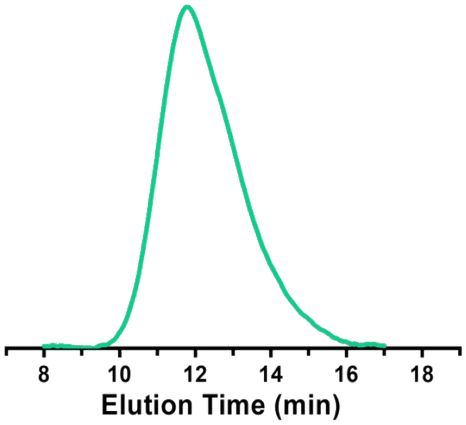

Figure S8. GPC traces of PDMA after a 150 minutes reaction. The reaction was conducted in deionized water using 2.11 M DMA and 0.5 wt% 4-NA under 420 nm irradiation.

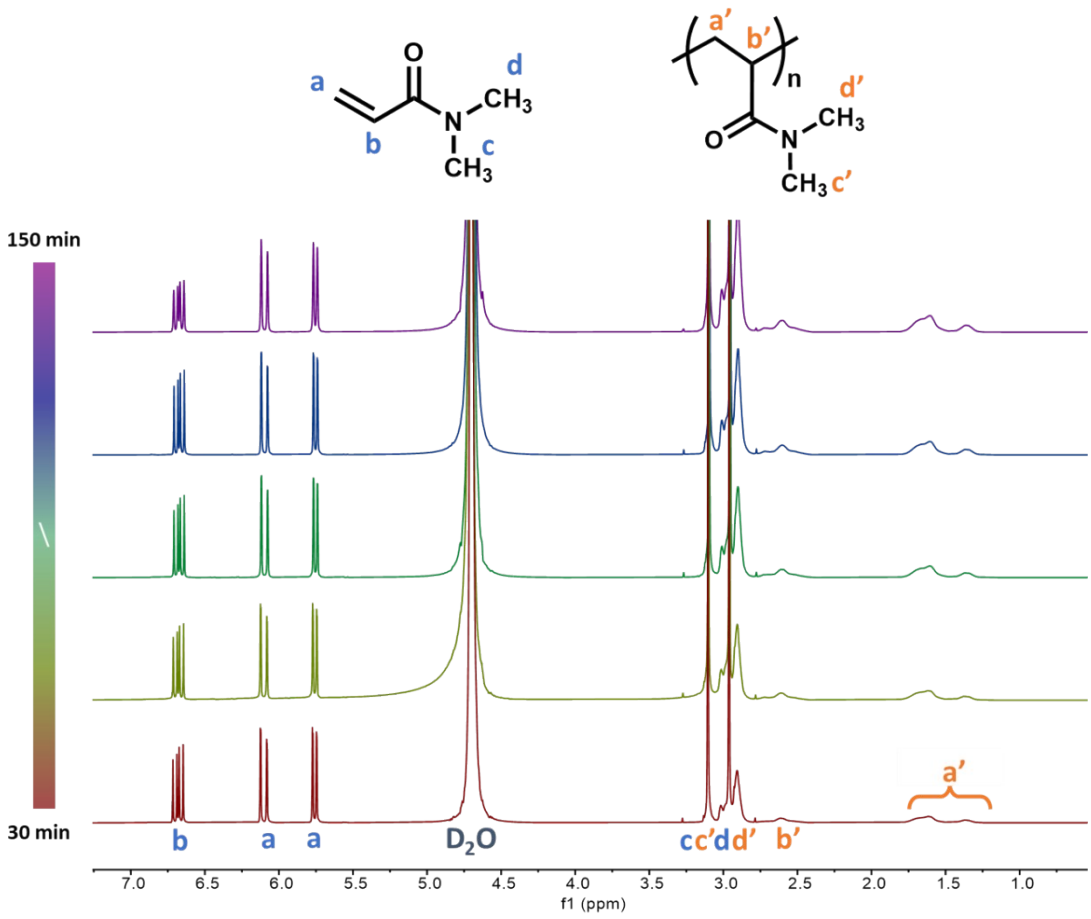

Figure S9. ^{1}H NMR spectra of DMA polymerization, which was carried out in deionized water using 2.11 M DMA and 0.5 wt% 4-NA, with the addition of 20 mM Ph_2ICl as a co-catalyst under 420 nm irradiation.

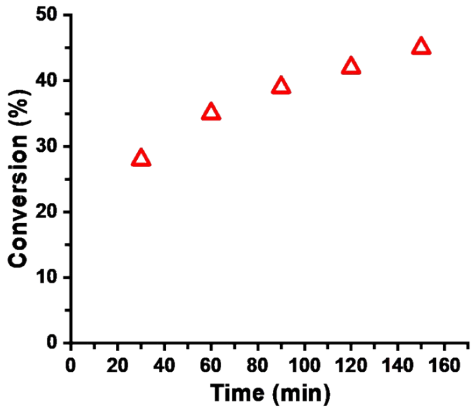

Figure S10. The evolution of monomer conversion according to reaction time. The reaction was carried out in deionized water using 2.11 M DMA and 0.5 wt% 4-NA, with the addition of 20 mM Ph_2ICl as a co-catalyst under 420 nm irradiation.

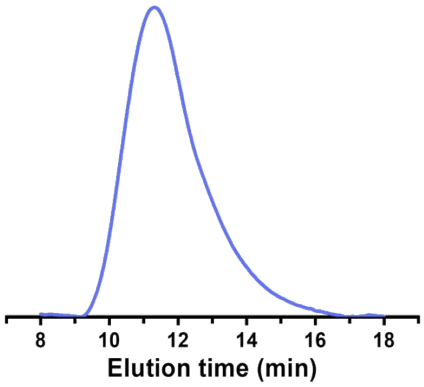

Figure S11. GPC traces of PDMA after a 150 minutes reaction. The reaction was conducted in deionized water using 2.11 M DMA and 0.5 wt% 4-NA, with the addition of 20 mM Ph_2ICl as a co-catalyst under 420 nm irradiation.

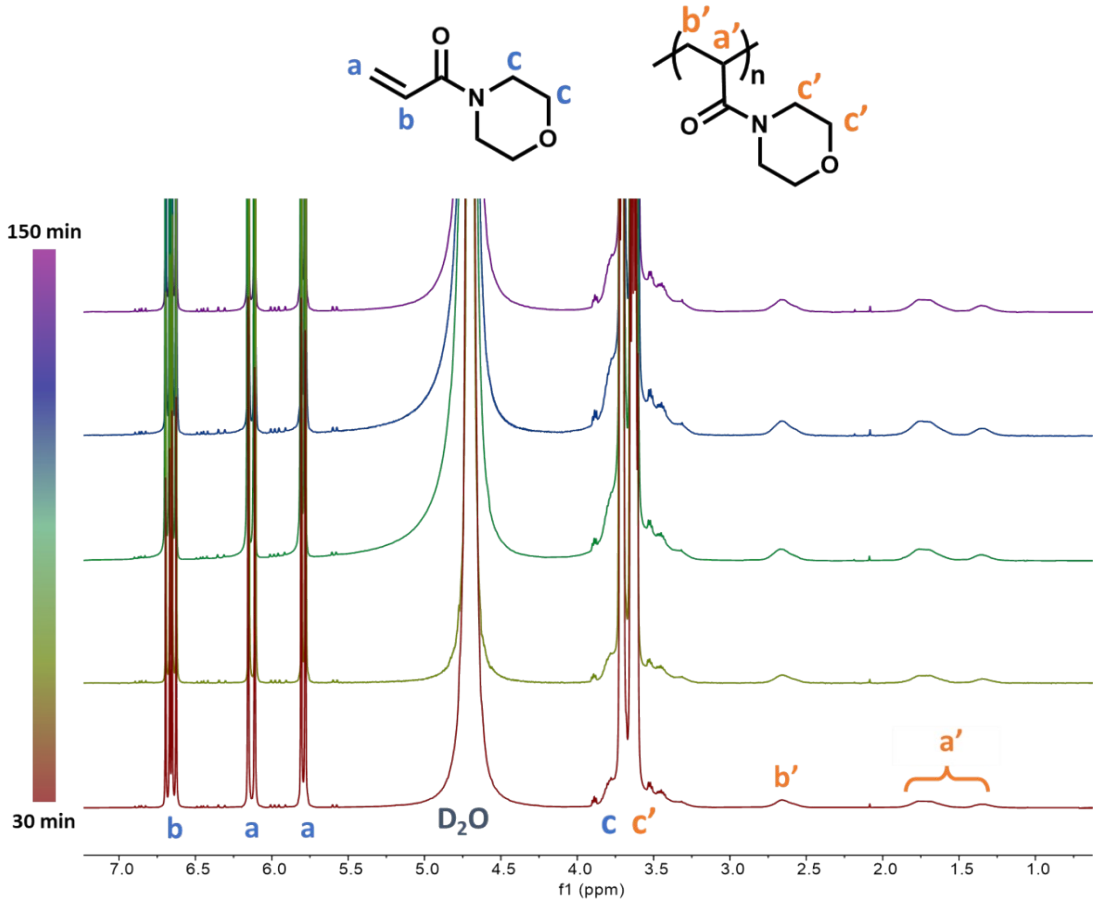

Figure S12. ^{1}H NMR spectra of AMP polymerization, which is carried out in deionized water using 2.11 M AMP and 0.5 wt% 4-NA, with the addition of 10 mM Ph_2ICl as a co-catalyst under 420 nm irradiation.

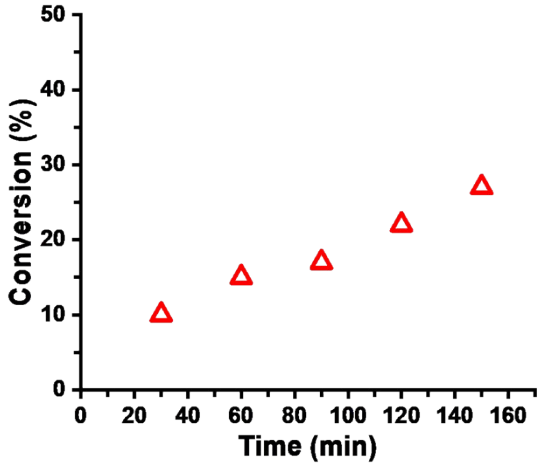

Figure S13. The evolution of monomer conversion according to reaction time. The reaction was carried out in deionized water using 2.11 M AMP and 0.5 wt% 4-NA, with the addition of 10 mM Ph_2ICl as a co-catalyst under 420 nm irradiation.

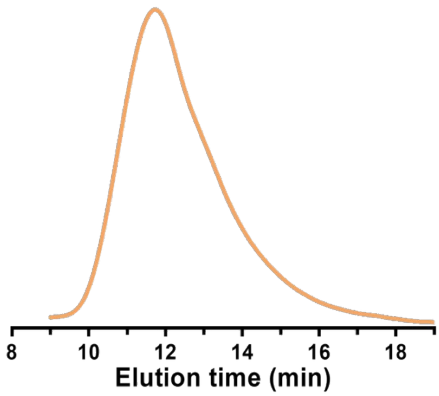

Figure S14. GPC traces of PAMP after a 150 minutes reaction. The reaction was conducted in deionized water using 2.11 M AMP and 0.5 wt% 4-NA, with the addition of 10 mM Ph_2ICl as a co-catalyst under 420 nm irradiation.

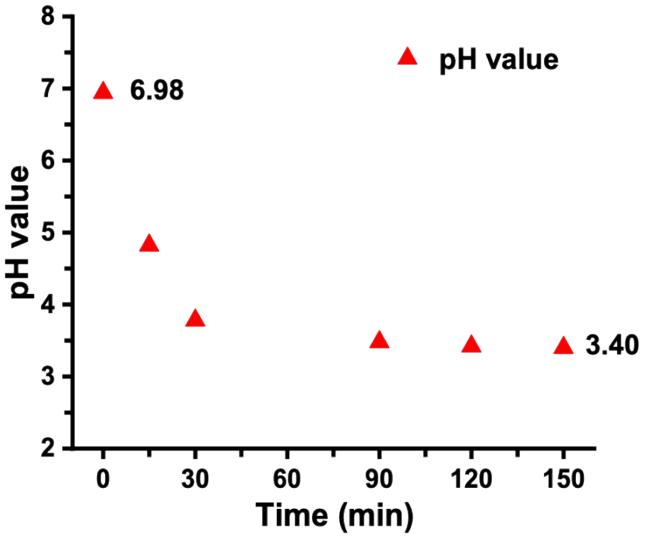

Figure S15. pH value of the reaction media in 150 min. The reaction was conducted when the initial concentration of Ph_2ICl and DMA were 10 mM and 2.11 M, respectively, with 0.5 wt% of 4-NA upon 420 nm irradiation at ambient temperature.

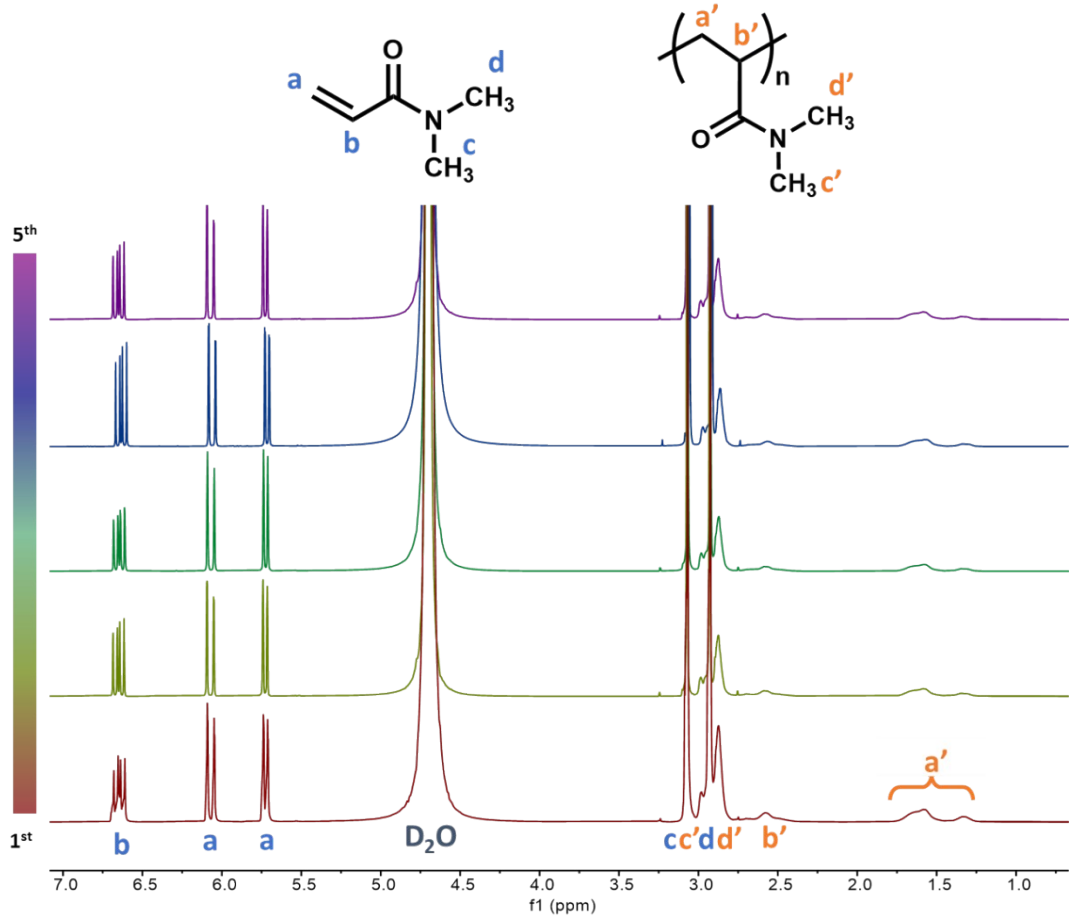

Figure S16. ^{1}H NMR spectra of DMA polymerization for the 4-NA reusing experiments.

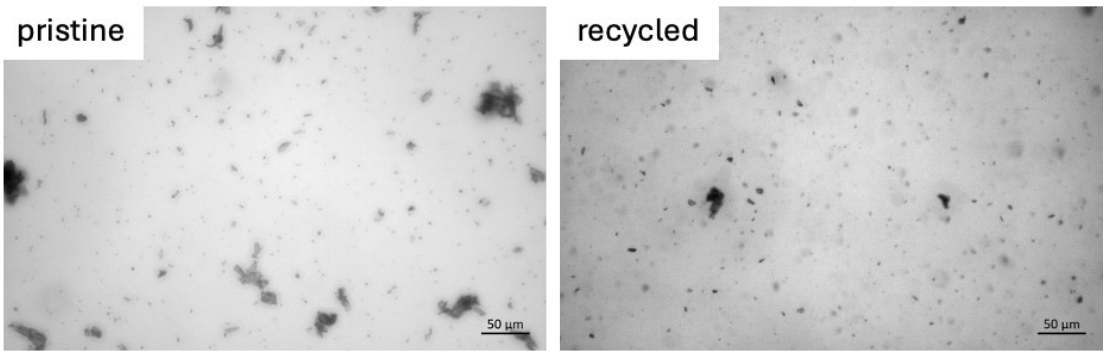

Figure S17. Optical image of pristine and recycled 4-NA.

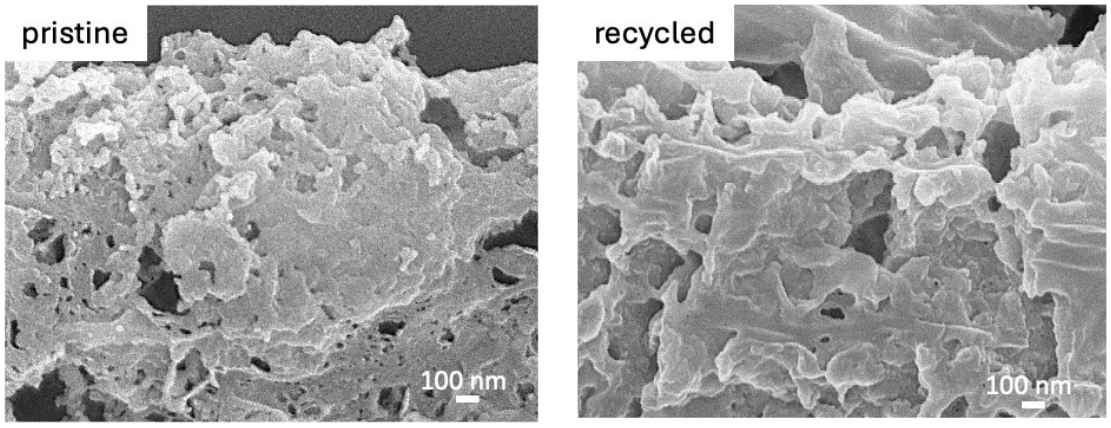

Figure S18. SEM image of pristine and recycled 4-NA.

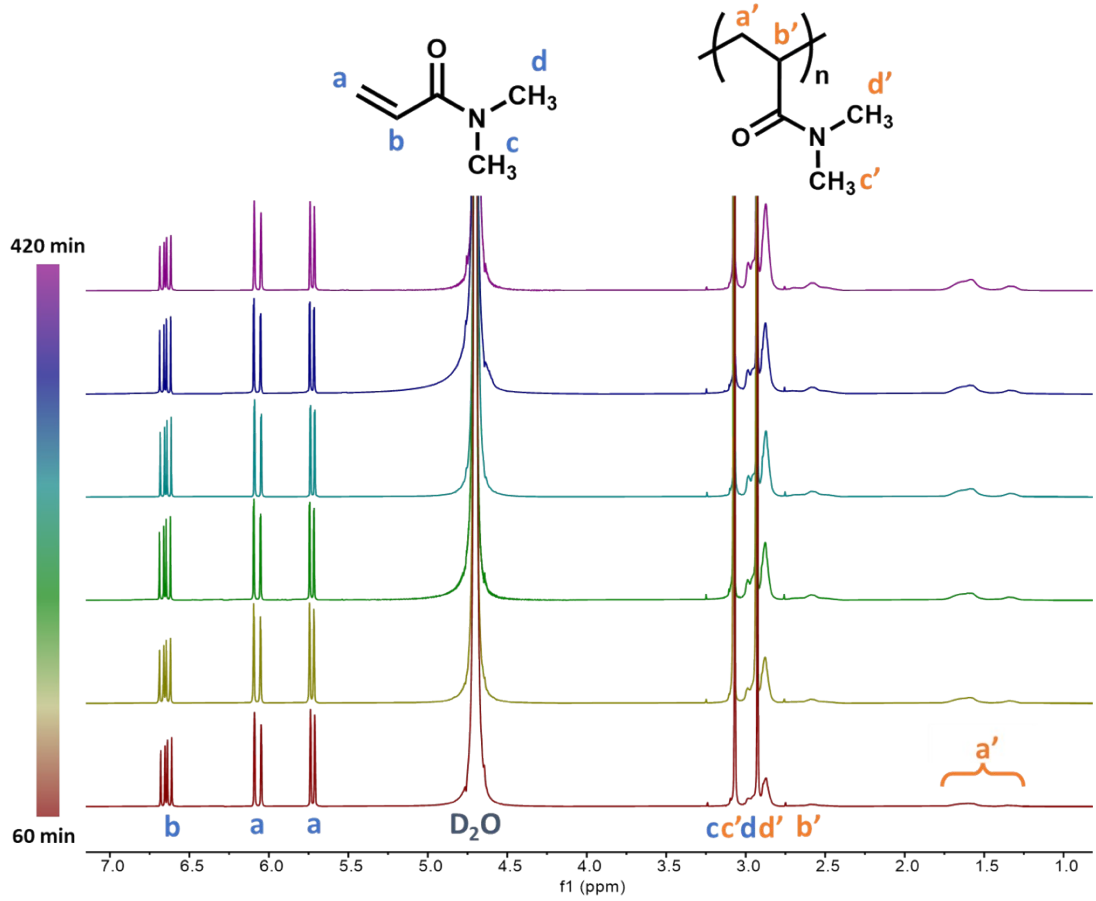

Figure S19. ^{1}H NMR spectra of photoinduced RAFT polymerization of DMA.

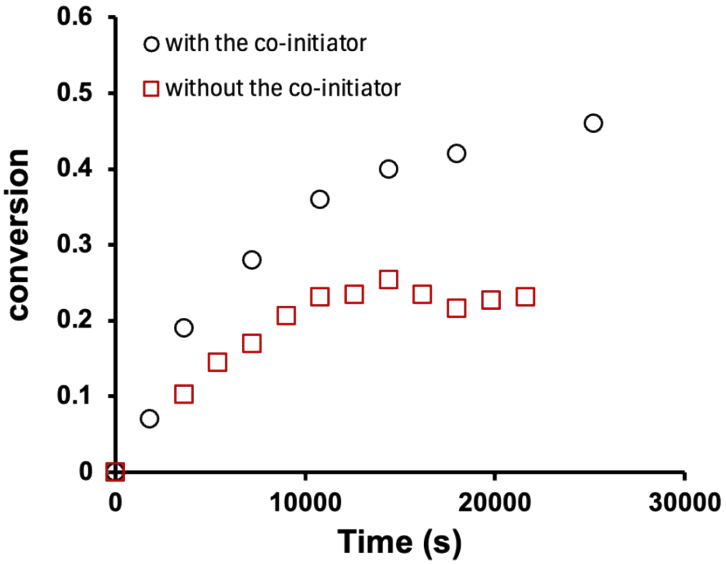

Figure S20. The evolution of monomer conversion according to reaction time for the RAFT polymerization with (circles) and without (squares) the co-initiator.