

Supporting Information:

Photolabile Protecting Groups: A Strategy for Making Primary Amine Polymers by RAFT

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Experimental Section

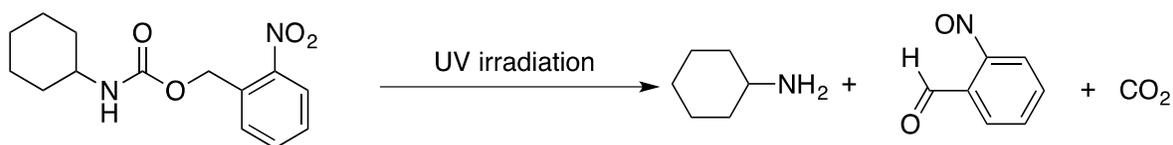
Materials

All reagents were obtained from commercial sources unless otherwise specified. All reagents were used as received unless otherwise specified. 2-Cyano-2-propyl benzodithioate (CPDB) was synthesized using a procedure outlined in the literature.¹

Synthesis of 2-nitrobenzylcyclohexyl carbamate

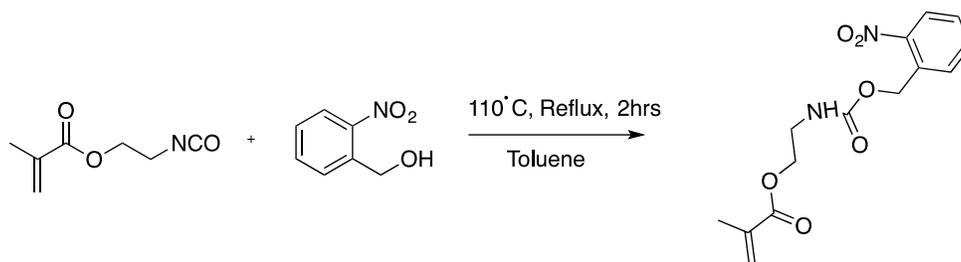
Synthesis of 2-nitrobenzylcyclohexyl carbamate was done according to previously studied procedure.² ¹H NMR (300 MHz, CDCl₃) δ 8.19 – 7.42 (m, 4H), 5.53 (s, 2H), 4.79 (d, *J* = 6.6 Hz, 1H), 3.62 – 3.40 (m, 1H), 2.08 – 1.06 (m, 11H).

Deprotection of photo protective group from 2-nitrobenzylcyclohexyl carbamate



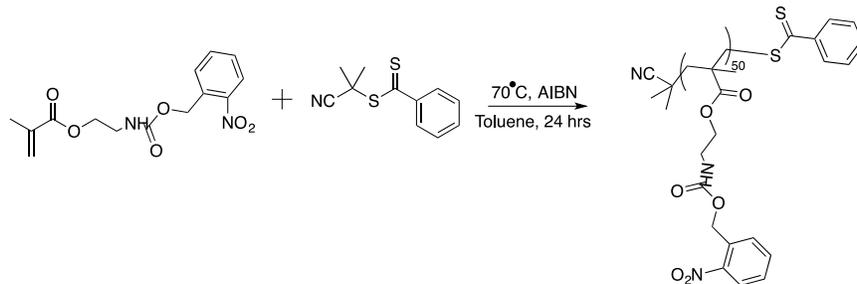
In a typical deprotection of ONBCC, to an NMR tube, 0.020g of ONBCC was dissolved in 1.0mL of CDCl₃. Corresponding mixtures were irradiated with 310nm, 392nm, 440 nm, 520 nm and 630 nm wavelengths and analyzed through NMR at 0 h, 2 h, 4 h, 8 h, 16 h, and 24 h.

Synthesis of 2-{{(benzyloxy)carbonyl}amino}ethyl 2-methylprop-2-enoate (ONBAMA):



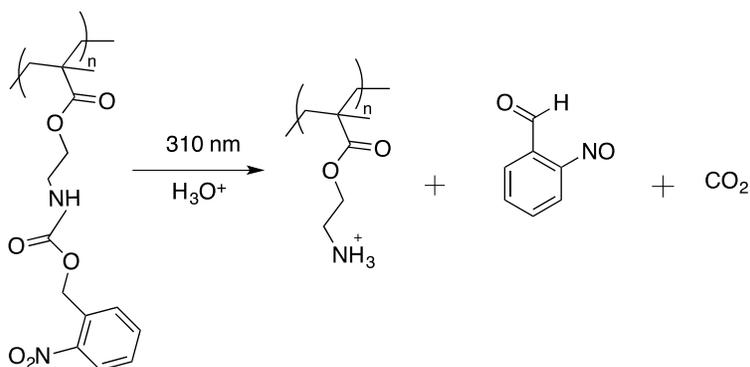
In a 10 mL two neck round bottom flask equipped with magnetic stirrer bar and a condenser, 2-nitrobenzylalcohol (2.50 g, 0.016 mol) and 2-isocyanatoethylmethacrylate (2.66 g, 0.017 mol) were added and dissolved in 5 mL toluene. The reaction mixture was deoxygenated for 15min and then temperature was increased up to 110 °C over 1 hour. Subsequently, the temperature was maintained between 110 °C-120 °C for 1.5 h, after which time the reaction was stopped. Mixture was then cooled to room temperature and precipitated with hexane to obtain off-white colored 2-{{(benzyloxy)carbonyl}amino}ethyl 2-methylprop-2-enoate monomer (ONBAMA) (4.52 g, 0.015mol, 90% yield). The compound was confirmed through ¹H NMR, ¹³C NMR, ESI/MS analysis. ¹H NMR (300 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 8.2 Hz, 1H), 7.74 – 7.46 (m, 3H), 5.90 (d, *J* = 157.1 Hz, 2H), 5.57 (s, 2H), 5.20 (s, 1H), 4.30 (t, *J* = 5.3 Hz, 2H), 3.58 (q, *J* = 5.7 Hz, 2H), 1.99 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 167.32, 155.76, 147.43, 135.90, 133.71, 132.99, 128.84, 128.61, 126.16, 124.98, 77.29, 77.04, 76.78, 63.58, 63.45, 40.41, 18.31. ESI/MS=331.1(monomer + Na⁺)

Synthesis of poly 2-{{(benzyloxy)carbonyl}amino}ethyl methacrylate poly(ONBAMA)



For a typical synthesis of poly(ONBAMA), to a 10 mL round bottom flask containing a stirrer bar, ONBAMA (1.00g, 3.25mmol), CPDB (0.018g, 0.006mmol), and Azobis(isobutyronitrile) (AIBN) (0.002g, 0.001mmol) were dissolved in 4 mL of toluene. The mixture was purged with N₂ for 15 min and then heated for 70 °C for 24 h. Polymer was obtained by precipitation into hexane. Precipitated polymers were characterized by SEC.

Deprotection of 2-nitro benzyl group from poly 2-{{(benzyloxy)carbonyl}amino}ethyl methacrylate



Poly[ONBAMA] (0.06 g, 0.19 mmol ONBAMA) and conc. HCl (0.011 g, 0.29 mmol HCl) were dissolved with 1 mL of DMSO. Solution was irradiated with 310 nm light in a NMR tube and upon irradiation NMR and SEC analysis were carried out at 0hr, 2 h, 4 h, 8 h, 16 h, and 24 h of irradiation times. Prior to SEC analysis, 0.100 mL volume of deprotected amine solution was neutralized with 0.004 g (with equal moles of HCl moles in 0.100mL).

Analytical Methods

Nuclear magnetic resonance (NMR) Spectroscopy

Nuclear magnetic resonance (NMR) measurements were carried out using Bruker 300 and 500 MHz spectrometers.

Mass Spectrometry

ESI-MS spectra data were collected using positive ion mode of Bruker Esquire-LC mass spectrometer (Billerica, MA).

UV-Visible Spectroscopy

UV measurements were collected using LAMBDA 750 UV/Vis/NIR Spectrophotometer

Size exclusion Chromatography (SEC)

Size exclusion chromatography (SEC) was performed to determine polymer molar mass data using an Agilent 1260 SEC system equipped with an auto-sampler, an Agilent 1260 isocratic pump, Agilent 1 guard and 2 analytical PolarGel-M columns, degasser and Agilent 1260 refractive index (RI detector). DMF was used as the eluent at 25 °C with a flow rate of 1 mL/min. All the samples were filtered before the injection to instrument.

Size distribution and Zeta Potential measurements

Size distribution measurements of the amine functionalized polymer was obtained using Zeta sizer ZEN1600 Nano series instrument at 25 °C. Zeta potential was measured using nanobrook ZetaPlus zeta potential analyzer. Each solution (1.3mg/mL) was passed through 0.22 µm filter.

Photo reactor Characterization

All the intensities of UV and visible light sources were determined using ThorLabs PM100A light power meter.^{3, 4}

Supplemental Data

Photoreactor data

Table S1: Characterization for the Visible light (Violet, Blue, Green, and Red)⁴ and Ultraviolet³ photoreactors. The wavelength of peak emission (λ_{\max}), Full width at half maximum (FWHM), and power output intensity (I) are given. Uncertainty in λ_{\max} is estimated at half the FWHM rounded to 1 significant figure, with a minimum uncertainty of 10 nm.⁴

Reactor	λ_{\max} (nm)	FWHM (nm)	I (mW/cm ²)
Ultraviolet	310 ± 20	40	49 ± 5
Violet	390 ± 10	10	3.7±0.3
Blue	440 ± 10	20	11.6±0.3
Green	520 ± 20	30	5.9±0.3
Red	630 ± 10	20	4.7±0.3

UV-Visible Spectra Analysis

A 0.25mM 2-nitrobenzylcyclohexyl carbamate solution was prepared in chloroform and the UV-Visible spectra was measured over the time of irradiation to 310nm UV light. (0min, 5min, 10min, 15min, 20min, 25min, 30min and 45min)

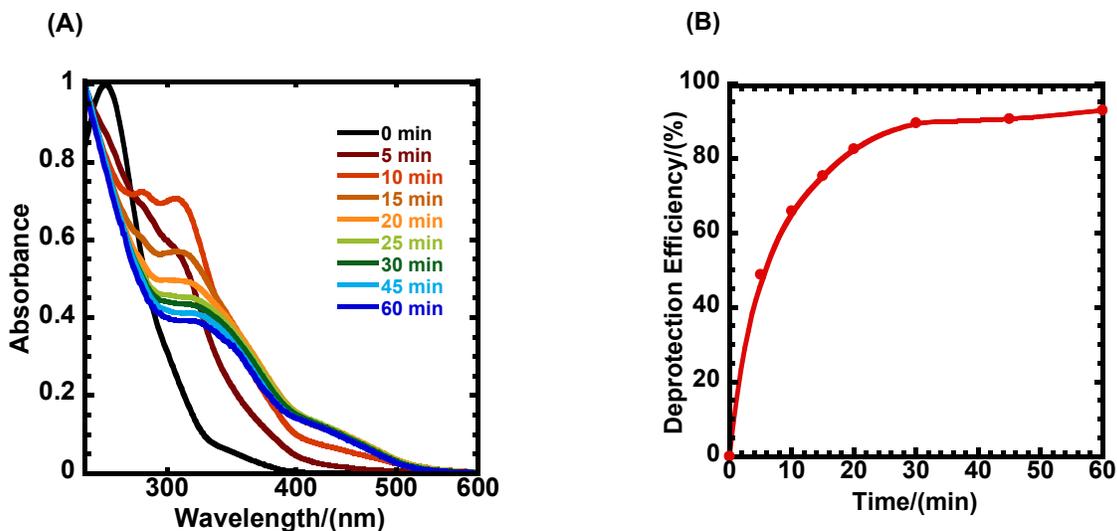


Figure S1: A). Changes in UV-Visible spectra of ONBCC upon irradiation under UV irradiation ($\lambda_{\max} = 310 \pm 20$ nm, $I = 49 \pm 5$ mW/cm²) over time (0min, 5 min, 10 min, 15 min, 20 min, 25 min, 30 min 45 min and 60 min) at r.t, [ONBCC]=0.25mM. B). Kinetics measured by NMR, of photochemical deprotection under UV irradiation ($\lambda_{\max} = 310 \pm 20$ nm, $I = 49 \pm 5$ mW/cm²) of ONBCC as a function of wavelength at r.t. [ONBCC] = 0.25 mM.

Table S2: Characterization of poly(ONBAMA) chains. Reaction Conditions, Time, Conversion, theoretical number averaged molar mass (M_{n-Th}), experimental number averaged molar mass (M_n), and molar mass dispersity (M_w/M_n) values are given.

	[ONBAMA]:[CPDB]:[AIBN]	Time	Conv.	k_p^{app}	M_{n-Th}	M_n	M_w/M_n
		(h)	(%)	(h ⁻¹)	(g/mol)	(g/mol)	
Low	25:1:0.2	16	97	0.22	7690	9200	1.27
(L)							
Medium	50:1:0.2	24	97	0.13	15159	16000	1.33
(M)							
High	100:1:0.2	24	95	0.11	29481	28000	1.34
(H)							

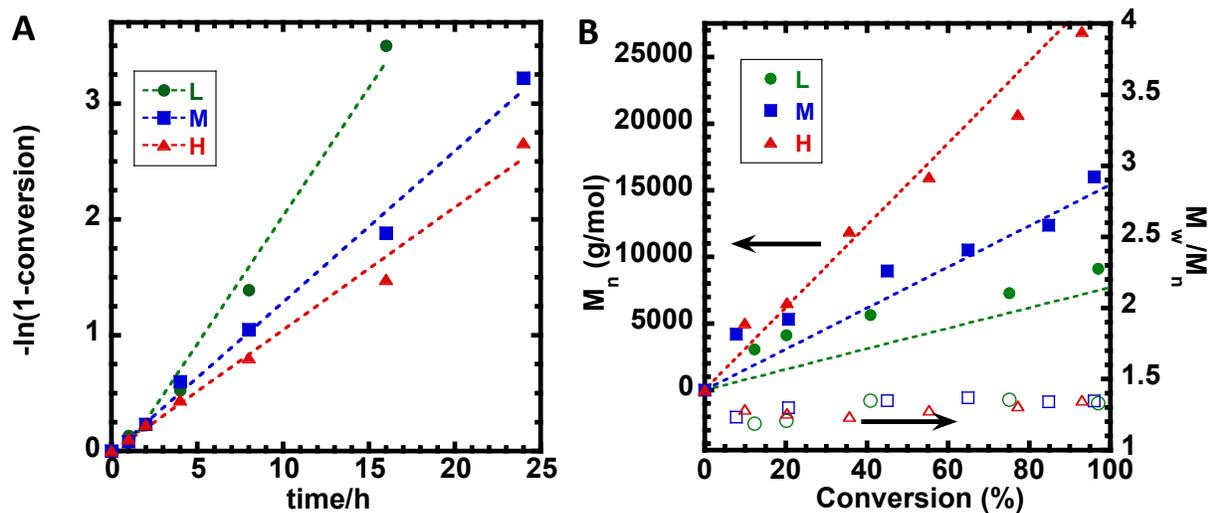


Figure S2: A) Semi- logarithmic kinetic plot and B) Evolution of M_n (solid points), M_{n-th} (dashed line), and M_w/M_n (hollow points) with conversion. Conditions: [ONBAMA]:[CPDB]:[AIBN] = X:1:0.2, where X =100 for H, 50 for M and 25 for L series, 1 g of ONBAMA in 4 mL of toluene at 70 °C.

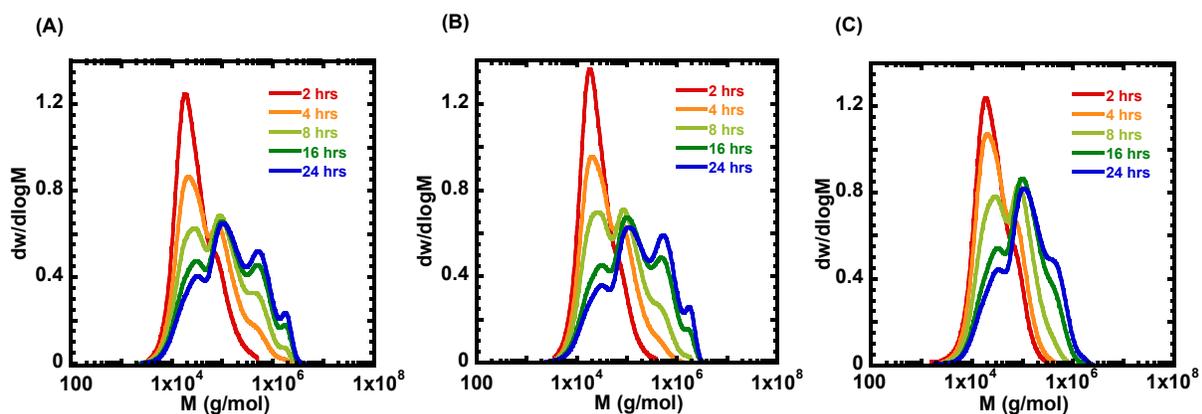


Figure S3: SEC molar mass distribution data for the poly(ONBAMA)₅₀ (60 mg/mL) over irradiation time (2 h, 4 h, 8 h, 16 h, 24 h) under UV irradiation ($\lambda_{max} = 310 \pm 20$ nm, $I = 49 \pm 5$ mW/cm²); A) Initial solution in DMSO with Amine functional groups: Acetic acid=1:1 ratio, B). Initial solution in DMSO with Amine functional groups: Acetic acid=1:2 ratio, C). Initial solution in DMSO with Amine functional groups: Acetic acid=1:10 ratio

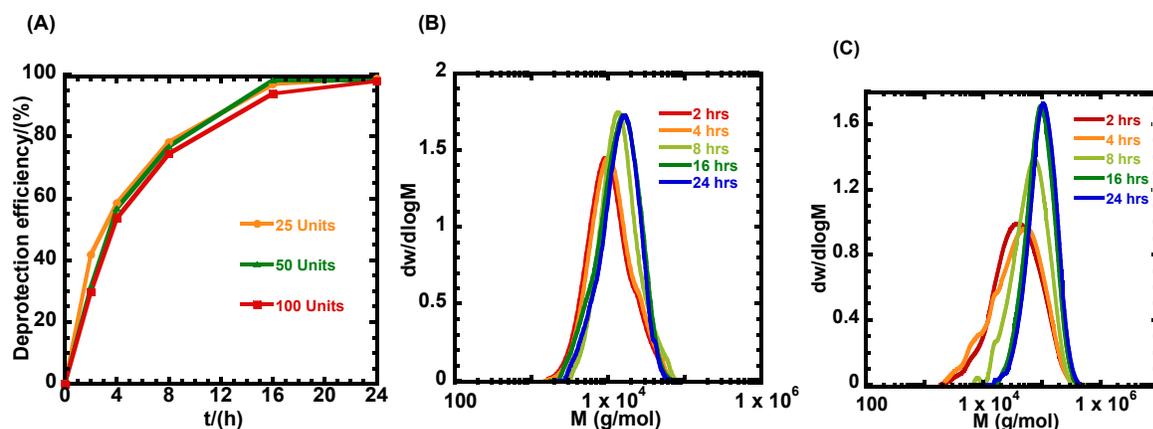


Figure S4: a) Deprotection efficiencies of poly(ONBAMA) of 25, 50, and 100 unit long polymer chains at r.t the polymer (60 mg/mL) over irradiation time (2 h, 4 h, 8 h, 16 h, 24 h) under UV irradiation ($\lambda_{\text{max}} = 310 \pm 20$ nm, $I = 49 \pm 5$ mW/cm²); b) SEC molar mass distribution data for the deprotection of initial solution of poly(ONBAMA)₂₅ in DMSO with Amine functional groups: HCl=1:1.5 ratio, under UV irradiation ($\lambda_{\text{max}} = 310 \pm 20$ nm, $I = 49 \pm 5$ mW/cm²) c). SEC molar mass distribution data for the deprotection of initial solution of poly(ONBAMA)₁₀₀ in DMSO with Amine functional groups: HCl=1:1.5 ratio under UV irradiation ($\lambda_{\text{max}} = 310 \pm 20$ nm, $I = 49 \pm 5$ mW/cm²).

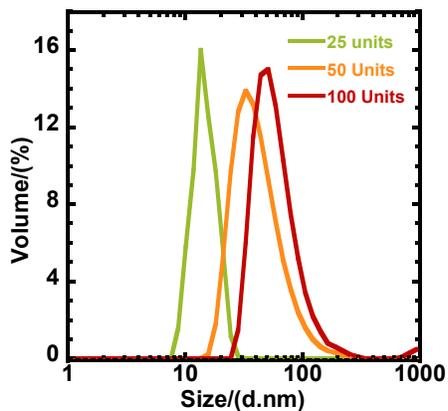


Figure S5: DLS data for deprotected ammonium functional 25, 50 and 100 unit polymer chains after 24 h of irradiation with 310 nm light at r.t with Amine functional groups: HCl=1:1.5 ratio, concentration = 1.34 mg/mL.

References

1. D. Konkolewicz, B. S. Hawkett, A. Gray-Weale and S. Perrier, *Macromolecules*, 2008, **41**, 6400.
2. M. R. Winkle, US Pat., 5650261 A, 1997.
3. J. A. Reeves, M. L. Allegranza and D. Konkolewicz, *Macromol. Rapid Commun.*, 2017, **38**, 1600623.
4. M. L. Allegranza, Z. M. DeMartini, A. J. Kloster, Z. A. Digby and D. Konkolewicz, *Polym. Chem.*, 2016, **7**, 6626.