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-nitrobenzyl alcohol (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 15 min 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, 0.015 mol, 90% yield). The compound was confirmed through $^1$H NMR, $^{13}$C NMR, ESI/MS analysis. $^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 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). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 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 N\textsubscript{2} 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 Zetasizer 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) and Ultraviolet photoreactors. The wavelength of peak emission ($\lambda_{\text{max}}$), Full width at half maximum (FWHM), and power output intensity ($I$) are given. Uncertainty in $\lambda_{\text{max}}$ is estimated at half the FWHM rounded to 1 significant figure, with a minimum uncertainty of 10 nm.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>FWHM (nm)</th>
<th>$I$ (mW/cm$^2$)</th>
</tr>
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<tbody>
<tr>
<td>Ultraviolet</td>
<td>310 ± 20</td>
<td>40</td>
<td>49 ± 5</td>
</tr>
<tr>
<td>Violet</td>
<td>390 ± 10</td>
<td>10</td>
<td>3.7±0.3</td>
</tr>
<tr>
<td>Blue</td>
<td>440 ± 10</td>
<td>20</td>
<td>11.6±0.3</td>
</tr>
<tr>
<td>Green</td>
<td>520 ± 20</td>
<td>30</td>
<td>5.9±0.3</td>
</tr>
<tr>
<td>Red</td>
<td>630 ± 10</td>
<td>20</td>
<td>4.7±0.3</td>
</tr>
</tbody>
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**UV-Visible Spectra Analysis**

A 0.25mM 2-nitrobenzylecyclohexyl 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 ($\lambda_{\text{max}} = 310 \pm 20$ nm, $I = 49 \pm 5$ mW/cm$^2$) over time (0 min, 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 ($\lambda_{\text{max}} = 310 \pm 20$ nm, $I = 49 \pm 5$ mW/cm$^2$) 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 ($M_{n-\text{Th}}$), experimental number averaged molar mass ($M_n$), and molar mass dispersity ($M_w/M_n$) values are given.

<table>
<thead>
<tr>
<th>[ONBAMA]:[CPDB]:[AIBN]</th>
<th>Time</th>
<th>Conv.</th>
<th>$k_p^{\text{app}}$</th>
<th>$M_{n-\text{Th}}$</th>
<th>$M_n$</th>
<th>$M_w/M_n$</th>
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<tr>
<td>Low</td>
<td>25:1:0.2</td>
<td>16</td>
<td>97</td>
<td>0.22</td>
<td>7690</td>
<td>9200</td>
</tr>
<tr>
<td>(L)</td>
<td></td>
<td></td>
<td>(h)</td>
<td>(%)</td>
<td>(g/mol)</td>
<td></td>
</tr>
<tr>
<td>Medium</td>
<td>50:1:0.2</td>
<td>24</td>
<td>97</td>
<td>0.13</td>
<td>15159</td>
<td>16000</td>
</tr>
<tr>
<td>(M)</td>
<td></td>
<td></td>
<td>(h)</td>
<td>(%)</td>
<td>(g/mol)</td>
<td></td>
</tr>
<tr>
<td>High</td>
<td>100:1:0.2</td>
<td>24</td>
<td>95</td>
<td>0.11</td>
<td>29481</td>
<td>28000</td>
</tr>
<tr>
<td>(H)</td>
<td></td>
<td></td>
<td>(h)</td>
<td>(%)</td>
<td>(g/mol)</td>
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**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 ($\lambda_{\text{max}} = 310 \pm 20$ nm, $I = 49 \pm 5$ mW/cm$^2$); 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/cm$^2$); 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/cm$^2$) 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/cm$^2$).

**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