Spatial and Temporal Control of Thiol-Michael Addition via Photo-caged Amine in Photopatterning and Two-stage Polymer Networks Formation

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SUPPORTING INFORMATION

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General Information:

Unless otherwise noted, all reactions were run under air. All chemical reagents were obtained commercially without further purification. $^1$H and $^{13}$C NMR spectra were recorded on Bruker Avance-III 400 spectrometers. Mass spectral and analytical data were obtained via the PE SCIEX/ABI API QSTAR Pulsar Hybrid LC/MS/MS, Applied Biosystems operated in the central analytical laboratory, University of Colorado at Boulder. Infrared (IR) spectra were recorded on a Thermo Nicolet Avatar 370 FT-IR spectrometer.

Experimental:

1. General Procedure

1.1 Synthesis photolabile amines (NVOC/NPPOC-NR$_1$R$_2$)
1.2. Photolysis of photolabile amines and photochemical properties determination.

**Photo-irradiation Experiment:** All photobases were dissolved in MeOH and then stirred under 320-390 nm irradiation (20mW/cm²) for 1 hour. A real time UV-Vis scan was applied to acquire UV-Vis data points (scanning 1nm/s from 200 to 600nm).

**Calculation of quantum yield of base generation (Φ₇)**

\[
Φ₇ = \frac{\text{rate of photobase generator consumed}}{\text{rate of photon absorption}} = \frac{\text{rate of base production}}{\text{rate of photon absorption}}
\]

Where rate of photon absorption is expressed as moles of photons absorbed per unit volume per unit time.

Using a fiber-coupled UV-Vis dispersive spectrometer (Thermo-Scientific) we remotely monitored changes in the 300-450 nm region of the electromagnetic spectrum during irradiation of samples in a cuvette holder. Peaks related to the consumption of the photobase generators (NVOC-R, and NPOC-R), where R= HEA, DEA or TMG, as well as the formation of the cleavage products are found within this region. Hence, isosbestic points were found for all photobase generators in methanol as the photolabile groups are cleaved from protecting group.
Figure S2. NPPOC-DEA photobleaching in methanol under 320-390 nm irradiation at 20 mW/cm². Left- Absorbance versus wavelength spectrum. Right- Photobase concentration decay with time using 400 nm as probing wavelength.

From these results we selected 335 nm and 400 nm as the wavelengths of interested for the calculation of the rates. Then, by analyzing the change in absorbance with time at these wavelengths we obtained the initial rate of photobase consumption and/or the initial rate of base generation (moles per volume per time).

Figure S3. Normalized concentration of photobase generators as a function of time under continuous irradiation at 20 mW/cm² with 320-390 nm irradiation.

On the other hand, a linear CCD array spectrophotometer (Ocean Optics) was utilized to obtain a measurement of the irradiance spectrum from the mercury arc lamp using a 320-390 nm filter.
Figure S4. Comparison of absorbance spectra and emission spectra for the photobase generators and the mercury arc lamp used with a 320-390 nm band pass filter.

The photon count vs wavelength data was converted into power density using Planck’s law \( (E=N_A \cdot \nu \cdot h) \) and adjusting for the non-linear response in the spectrophotometer. With this power density reading, the incident light at the surface of the solution for each wavelength is determined.

To account for light attenuation we calculated the average light transmission through the depth of the solution. \( C_{\text{avg}} \) is the average photobase concentration during the time span (900 s) from which the average rate of consumption was determined; thus, accounting for the different changes in absorbance with time.

\[
I = I_0 \cdot e^{-2.3 \cdot \varepsilon \cdot C_{\text{avg}} \cdot z}
\]

from which the average transmitted light is given by

\[
I_{\text{avg}} = \frac{\int_{z_1}^{z_2} I_0 \cdot e^{-2.3 \cdot \varepsilon \cdot C_{\text{avg}} \cdot z} \, dz}{\int_{z_1}^{z_2} \, dz}
\]

solving the integral analytically we obtain

\[
I_{\text{avg}} = \left( \frac{I_0}{2.3 \cdot \varepsilon \cdot C_{\text{avg}}} \right) \cdot \left( 1 - e^{-2.3 \cdot \varepsilon \cdot C_{\text{avg}} \cdot z} \right) / (z_2 - z_1)
\]

evaluating \( z \) over the depth of the solution we obtain a light transmission \( (I'_{\text{avg}}) \) value at each wavelength within the irradiation envelope.

Then, the average light absorbed \( (I''_{\text{avg}}) \) was calculated by
\[ I'_{avg} = I_0 - I_{avg} \]

From these results, we then converted the absorbed light from Watts/cm\(^2\) to moles of photons per liter per second using \( I''_{avg} \):

\[ I''_{avg} = \frac{I'_{avg} \cdot \lambda}{0.1196 + z} \]

Since \( I''_{avg} \) changes with wavelength we summed the values from 301 to 420 nm to obtain an estimated total amount of photons absorbed per volume per time.

Finally, the quantum yield is obtained from

\[ \phi_b = \frac{R_{base}}{I''_{avg}} \]

where \( R_{base} \) comes from the slope of the concentration vs time plots for the first 900 s of reaction.

Table S1. Photochemical properties for photolabile bases.

| Photobase       | Photons (moles/L*s) | Rate (moles/L*s) | Quantum Yield (\(\Phi_b\)) | \(\varepsilon\) (368 nm) |
|-----------------|---------------------|------------------|-----------------------------|--------------------------|
| NPPOC-DEA       | 1.42E-06            | 2.86E-07         | 0.2014                      | 196                      |
| NVOC-DEA        | 1.58E-05            | 1.34E-07         | 0.0085                      | 1776                     |
| NPPOC-TMG       | 1.73E-06            | 2.59E-07         | 0.1497                      | 240                      |
| NVOC-TMG        | 1.78E-05            | 1.32E-07         | 0.0074                      | 1988                     |
| NPPOC-HEA       | 1.22E-05            | 1.16E-08         | 0.0010                      | 4600                     |
| NVOC-HEA        | 4.32E-05            | 5.50E-08         | 0.0013                      | 4780                     |

1.3. Model photolabile bases catalyzed thiol-acrylate addition

To a 10 ml glass vial was added thiol (2mmol) and catalyst (0.1mmol) and to this was added Michael acceptor (Ethyl acrylate, Methyl Methacrylate, Divinylsulfone) (2mmol) in the dark. The mixture was vortexed until fully mixed. The mixture was then stirred under 320-390 nm irradiation (20mW/cm\(^2\)).

\[ \text{BuO} \longrightarrow \text{S} \longrightarrow \text{O} \longrightarrow \text{CO} \]

1. **Ethyl 3-((2-butoxy-2-oxoethyl)thio)propanoate**: \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 4.22 – 4.07 (m, 4H), 3.23 (s, 2H), 2.90 (t, \(J = 7.3\) Hz, 2H), 2.63 (t, \(J = 7.3\) Hz, 2H), 1.68 – 1.55 (m, 2H), 1.45 – 1.28 (m, 2H), 1.25 (t, \(J = 7.1\) Hz, 3H), 0.92 (t, \(J = 7.4\) Hz, 3H).
Ethyl 3-(hexylthio)propanoate: $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 4.14 (q, $J = 7.1$ Hz, 2H), 2.81 – 2.72 (t, $J = 7.2$ Hz, 2H), 2.62 – 2.47 (m, 4H), 1.61 – 1.50 (m, 2H), 1.44 – 1.19 (m, 6H), 0.87 (t, $J = 6.9$ Hz, 3H).

Methyl 3-((2-butoxy-2-oxoethyl)thio)-2-methylpropanoate: $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 4.19 – 4.08 (m, 2H), 3.69 (s, 3H), 3.21 (s, 2H), 3.00 – 2.87 (m, 2H), 2.82 – 2.66 (m, 2H), 1.70 – 1.57 (m, 1H), 1.46 – 1.31 (m, 3H), 1.29 – 1.20 (m, 3H), 0.93 (t, $J = 7.4$ Hz, 3H).

Ethyl 3-(phenylthio)propanoate: $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.43 – 7.16 (m, 5H), 4.14 (q, $J = 7.1$ Hz, 2H), 3.17 (t, $J = 7.4$ Hz, 2H), 2.62 (t, $J = 7.4$ Hz, 3H), 1.25 (t, $J = 7.1$ Hz, 3H).

Ethyl 3-((2-hydroxyethyl)thio)propanoate: $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 4.16 (q, $J = 7.1$ Hz, 2H), 3.74 (t, $J = 4.7$ Hz, 2H), 2.85 – 2.71 (m, 4H), 2.61 (t, $J = 7.2$ Hz, 2H), 1.27 (t, $J = 7.1$ Hz, 3H).

Dibutyl 2,2’-((sulfonylbis(ethane-2,1-diyl))bis(sulfanediyl))diacetate: $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 4.14 (t, $J = 6.7$ Hz, 4H), 3.43 – 3.32 (m, 4H), 3.28 (s, 4H), 3.13 – 3.03 (m, 4H), 1.70 – 1.58 (m, 4H), 1.46 – 1.32 (m, 4H), 0.94 (t, $J = 7.4$ Hz, 6H).

1.4. Kinetics study
Figure S2: (A) Conversion of stoichiometric Butyl thiolglycolate and Ethyl acrylate, 5mol% NPPOC-TMG, under continuous 320-390 nm irradiation (predominately the I-line of Hg) monitored by FTIR. (B) Thiol-conversion of stoichiometric Butyl thiolglycolate and Ethyl Acrylate with continuous irradiation and 0.5 min irradiation.
3. NMR Spectra
