

Supporting Information

Comprehensive High-throughput Screening of Photopolymerization under Light Intensity Variation using Inline NMR Monitoring

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Materials

Chemicals

The monomers methyl methacrylate (MMA, 99% Merck Pty Ltd), ethyl methacrylate (EMA, 99% Merck Pty Ltd), and butyl methacrylate (BMA, 99% Merck Pty Ltd) were purified over a column of activated basic alumina before use. 4-cyano-4- [(dodecyl sulfanyl thiocarbonyl) sulfanyl] pentanoic acid (CDP-TTC, 97% Boron molecular) and 3- (((1-carboxyethyl) thio) carbonothioyl) thio) propanoic acid (CTTP, 95% Boron molecular) were used as received. 2(((dodecylsulfanyl)carbonothioyl) sulfanyl) propanoic acid (DoPAT) and 4-cyano-4- [(carboxylsulfanyl thiocarbonyl) sulfanyl] pentanoic acid (CCP-TTC) were synthesized according to the literature.^{1, 2} 1,1'-azobis(isobutyronitrile) (AIBN, 98% Sigma-Aldrich) was recrystallized twice from methanol before use. Dimethyl sulfoxide (DMSO, 99% Chem-Supply Pty Ltd) was used as received.

Reactor Set-up

The tubular reactor ($V_{\text{reactor}} = 0.9 \text{ mL}$) setup consists of PFA tubing (1/16" OD, 0.75 mm ID) wrapped around a glass framework and placed in an oil bath heated up to 90°C on an IKA stirrer hot plate. The blue light LEDs (ILA-HSINK-STAR-50-20 mm) connected with the programmable variable DC power supply (RS PRO, RS-3005P, 0-30V, 0-5A) unit is placed above the glass framework at a distance of 45 mm. The intensity of blue light is measured using an optical power meter (Model- S401C, Pmax- 1W, Wave- 0.19-20 μm , Thorlabs). Reaction solutions are pumped into the reactor via a Fusion 100 classic syringe pump, using 10 mL SGE gastight syringes, preflushed with N₂. The flow rates for the time sweeps were pre-programmed via self-written software (Python and LabView).³

Table S 1 Overview of flow parts used in the reaction setup

	<p>IDEX XP-230</p>	<p>Flangeless Fitting Natural, PEEK, 1/4- 28 Flat-Bottom, for 1/16" OD</p>
	<p>IDEX F-120</p>	<p>One-Piece Finger tight 10-32 Coned, for 1/16" OD Natural</p>
	<p>IDEX P-629</p>	<p>Luer Adapter Female Luer x 10-32 Female, Tefzel™ (ETFE) Natural</p>
	<p>IDEX P-702</p>	<p>Union Assembly PEEK .020 thru hole, for 1/16" OD"</p>



Figure S 1 The image of LED (ILA-HSINK-STAR-50*20 mm) used in the photo flow experiments.

Intensity measurement of blue LED using an optical power meter.

Light intensities were measured using a ThorLabs PM400 Optical Power Meter equipped with a ThorLabs S401C Thermal Power Sensor. A wavelength of 460 nm was used for measurements of light intensity, with the sensor located adjacent to the reactor tubing with the LED located above the reactor, simulating the experimental setup (Figure S4). The intensity was varied by controlling the LED current using an RS PRO RS3005P variable power supply.

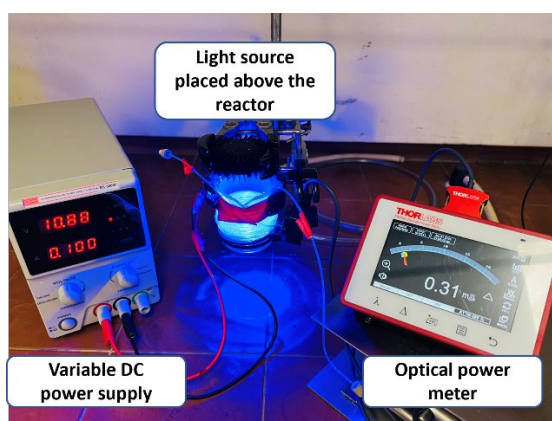


Figure S 2 The measurement set-up for light intensity with the optical power meter.

Table S 2 The intensity measured using the variable DC power supply and optical power meter.

Current (A)	Voltage (V)	Intensity (mW·cm⁻²)
0.05	10.68	1.45
0.10	10.92	2.30
0.25	11.38	4.60
0.30	11.45	5.35
0.35	11.58	6.03
0.40	11.69	6.69
0.50	11.91	7.95
0.75	12.43	10.82

Characterization

The inline ¹H NMR spectra were recorded using a low field benchtop NMR spectrometer (acquisition bandwidth 5 kHz: 83 ppm; 90 pulse width: 7 microseconds; dwell time: 200 microseconds; the number of points: 32,768; acquisition time: 6.554 seconds; repetition time: 17 seconds, 60 MHz, Magritek, Spinsolve Ultra, Germany). The spectrometer was shimmed using the standard solution of 10% D₂O in H₂O. Each spectrum was recorded every 17s, and the dead volume between the reactor and the benchtop NMR was 0.40 mL.

PSS SECcurity2 GPC systems operated by PSS WinGPC software, equipped with an SDV 5.0 µm guard column (50 x 8 mm), followed by three SDV analytical 5.0 µm columns with varying porosity (1000 Å, 100000 Å, and 1000000 Å) (50 x 8 mm) and a differential refractive index 3 detectors using THF as the eluent at 40 °C with a flow rate of 1 mL·min⁻¹. The GPC system was calibrated using linear narrow polystyrene standards from PSS Laboratories ranging from 682 to 2.52 x 10⁶ g·mol⁻¹ PS (K = 14.1 x 10⁻⁵ dL·g⁻¹ and α = 0.70).⁴ Molar masses of the pMMA samples were determined by universal calibration using Mark-Houwink-Sakurada (MHS) parameters for pMMA reported literature values (K = 12.9 x 10⁻⁵ dL·g⁻¹ and α = 0.68).⁵

Experimental Procedure

General photo-iniferter polymerization procedure

In a typical procedure, the monomer, photo-iniferter-agent, and solvent were added to a glass vial. The glass vial was sealed with a rubber septum and the solution was purged with nitrogen (N₂) for 5 minutes. Next, the reaction solution was transferred to a 10 mL gastight syringe (Trajan Scientific), preflushed with N₂, and placed in the holder of the syringe pump. A 0.9 mL tubular reactor is employed for the polymerization at a temperature of 90 °C under illumination with blue light (450 nm) with a timesweep measurement from 4 min to 12 min to 30 min³. Flowrates were defined by a python script, and commands were sent to the syringe pump via a Labview script. Monomer conversions were determined via ¹H NMR. Samples were directly collected from the reactor, and molecular weight distributions were measured via SEC.

NMR Data- Integral setting for conversion calculation.

The benchtop NMR gives absolute integral values in the output csv files. Generally used method for conversion calculation for screening is the solvent-butyl acetate method, which is clearly described in the literature, reported from our group⁶. The proper setting of integral and base-line correction is very important in calculating the correct conversion of different polymerization screening. Inappropriate integral setting can give wrong results to the experiments (sometimes negative conversions, which make no sense.) An example of importance of integral setting and base-line correction is given below.

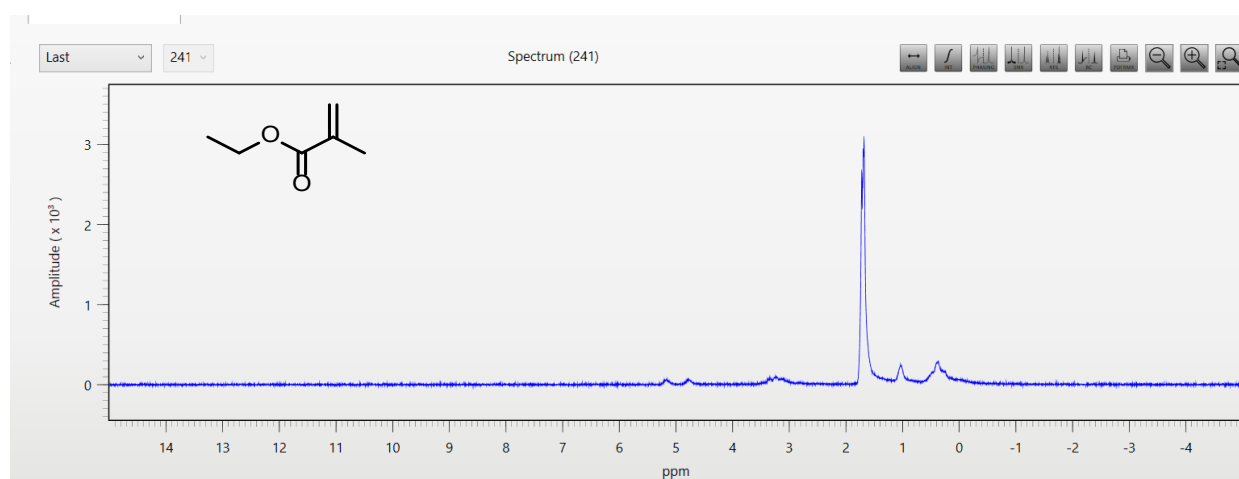


Figure S 3 The raw NMR spectra for 3 M ethyl methacrylate polymerization screening from spinsolve software, before setting any peaks.

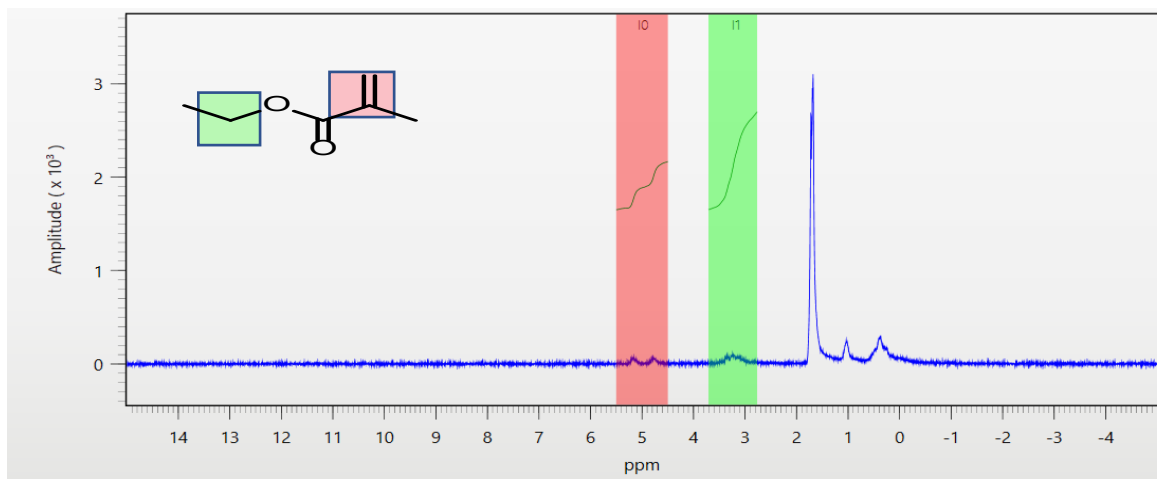


Figure S 4 Scan 45 from the NMR spectra of 3 M ethyl methacrylate polymerization at $1.45 \text{ mW} \cdot \text{cm}^{-2}$, i_0 (red): vinyl protons, i_1 (green): $-\text{CH}_2$ -protons from monomer and polymer. With $i_0=40.7$, and $i_1=46.6$, the monomer conversion was calculated as 12.6 % (at residence time of 9 min).

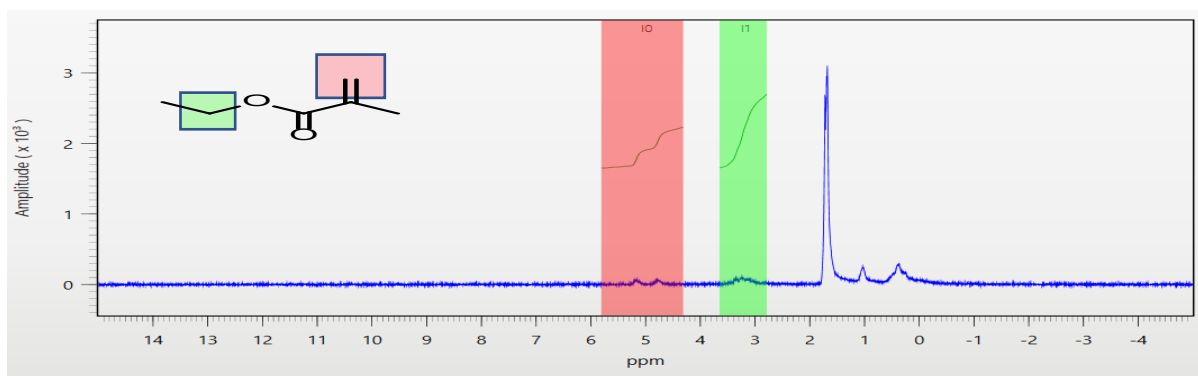


Figure S 5 Setting integral (without proper base-line correction) for the same scan 45 from the NMR spectra of 3 M ethyl methacrylate polymerization at $1.45 \text{ mW} \cdot \text{cm}^{-2}$, With $i_0=52.49$, and $i_1=51.487$, the monomer conversion was calculated as -2.0 % (at residence time of 9 min), which does not make any sense.

This is a very important observation during the polymerization screening through the NMR software. The operator should accurately and carefully set the relevant integration borders with proper base-line correction to calculating the exact final monomer conversion.

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