Electronic Supplementary Material (ESI) for Polymer Chemistry.

Assembly of a Visible Light Photoreactor: An Inexpensive Tool for Bottlebrush Polymer Synthesis via Photoiniferter Polymerization

Kyle J. Arrington and John B. Matson

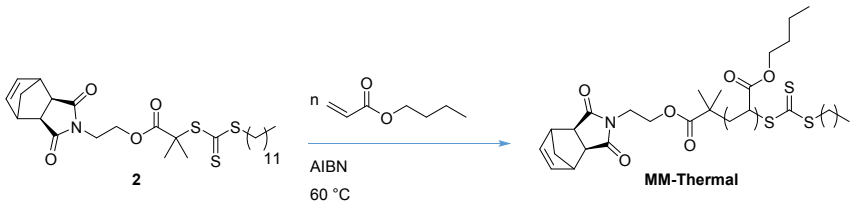
Department of Chemistry and Macromolecules Innovation Institute, Virginia Tech, Blacksburg, Virginia 24061, United States

Email: jbmatson@vt.edu

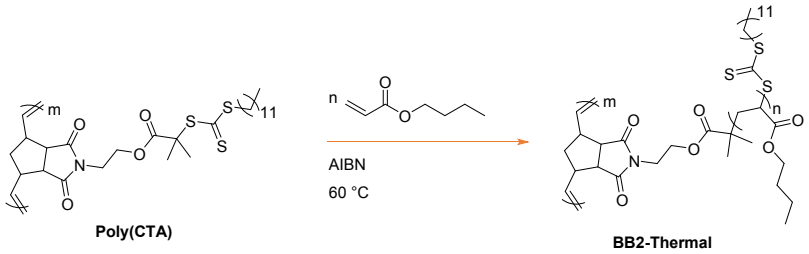
Materials and Methods

All chemical reagents were obtained from Sigma-Aldrich and used as received unless otherwise stated. Olefin metathesis catalysts were obtained as a generous gift from Materia. Trithiocarbonate I and CTA II were synthesized according to a previously published procedure.[1] NMR spectra were measured on an Agilent 400 MHz spectrometer. ^{1}H NMR chemical shifts are reported in ppm relative to internal solvent resonances. Size exclusion chromatography was carried out in THF at 30 °C on two Agilent PLgel 10 µm MIXED-B columns connected in series with a Wyatt Dawn Heleos 2 light scattering detector and a Wyatt Optilab Rex refractive index detector. No calibration standards were used, and d*n*/d*c* values were obtained by assuming 100% mass elution from the columns.

Schemes



Scheme S1. RAFT of *n*-butyl acrylate (nBA) with CTA **2**. Typical conditions: CTA **2** (1 equiv), AIBN (0.1 equiv), nBA (100 equiv), 1:1 v/v DMF to nBA. Reactions were run at 60 °C.



Scheme S2. Grafting-from RAFT of nBA with **Poly(CTA)**. Typical conditions: **Poly(CTA)** (1 equiv per CTA group), nBA (200 equiv per CTA group), 1:1 v/v DMF to nBA. Reactions are run at 60 °C.

Polymer Synthesis

Representative Procedure for Photoiniferter Polymerization

A 100 mL Schlenk tube was charged with a stir bar, DMF (4 mL), nBA (4 mL, 27.8 mmol), and photoiniferter **1** (101 mg, 0.277 mmol). The solution was then degassed by carrying out three freeze-pump-thaw cycles and backfilled with N_2. The reaction vessel was then placed inside the photoreactor on top of a stir plate. The light was then turned on by plugging the photoreactor into an outlet, and the reaction mixture was allowed to stir for up to 26 h (95% monomer conversion). The polymer product (MM-photo) was recovered by precipitation from methanol.

Note: Similar conditions were used to styrene, while for acryloylmorpholine (ACMO) monomer, 5 times the volume of solvent was used for the polymerization.

Representative Procedure for RAFT Polymerization

A 100 mL Schlenk tube was charged with a stir bar, DMF (4 mL), nBA (4 mL, 27.8 mmol), AIBN (4.54 mg, 0.0277 mmol) and photoiniferter **1** (101 mg, 0.277 mmol). The solution was then degassed by carrying out three freeze-pump-thaw cycles and backfilled with N_2. The reaction vessel was then placed in an oil bath set to 60 ^{o}C and allowed to stir for 12 h (95% monomer conversion). The polymer product (MM-thermal) was recovered by precipitation from methanol.

Representative Procedure for ROMP Grafting-Through

A vial was charged with a stir bar, THF (0.2 mL), and nBA macromonomer* (25 mg, 4.4 µmol). In a separate vial, a stock solution of **G3** was prepared in THF. An aliquot (50 µL) of the solution (0.032 mg, 0.044 µmol) was the injected into the reaction vial. The reaction mixture was allowed to stir for 1 h. A few drops of ethyl vinyl ether were then added to the reaction mixture to quench the polymerization. The bottlebrush polymer product was then recovered by precipitation from Et_2O.

*This macromonomer was prepared using the representative procedure for the photoiniferter polymerization or RAFT polymerization using photoiniferter **2**.

*Representative Procedure for ROMP of photoiniferter **2***

A vial was charged with a stir bar, THF (0.9 mL), and photoiniferter **2** (25 mg, 4.5 µmol). In a separate vial, a stock solution of **G3** was prepared in THF. An aliquot (100 µL) of the solution (0.17 mg, 0.23 µmol) was the injected into the reaction vial. The reaction mixture was allowed to stir for 1 h. A few drops of ethyl vinyl ether were then added to the reaction mixture to quench the polymerization. The product (**Poly-photoiniferter**) was then recovered by precipitation from Et2O.

Representative Procedure for Grafting-From using Photoiniferter Polymerization

A 100 mL Schlenk tube was charged with a stir bar, DMF (2.6 mL), nBA (2.6 mL, 18.06 mmol), and **poly-photoiniferter** (25 mg, 0.045 mmol in repeat unit). The solution was then degassed by carrying out three freeze-pump-thaw cycles and backfilled with N_2. The reaction vessel was then placed inside the photoreactor on top of a stir plate. The light was then turned on and the reaction mixture was allowed to stir overnight. The bottlebrush polymer was recovered by precipitation from methanol.

Representative Procedure for AIBN RAFT Grafting-From

A 100 mL Schlenk tube was charged with a stir bar, DMF (2.4 mL), nBA (2.5 mL, 18.06 mmol), and **poly-photoiniferter** (25 mg, 0.045 mmol in repeat unit). In a separate vial, a stock solution of AIBN was prepared in DMF. An aliquot (100 µL) of the solution (0.741 mg, 4.51 µmol) was then injected into the reaction vial. The solution was then degassed by carrying out three freeze-pump-thaw cycles and backfilled with N_2. The reaction vessel was then placed inside the photoreactor on top of a stir plate. The light was then turned on and the reaction mixture was allowed to stir with light overnight. The bottlebrush polymer product was recovered by precipitation from methanol.

Table S1: Itemized List

Item	Number of Uses	Total Cost	Cost per photoreactor
Heatsink	2	$8.65	$4.33
Power Adapter	1	$9.81	$9.81
Thermal Adhesive	10	$11.98	$1.20
Alligator Clips to Female DC Cable	1	$1.59	$1.59
Blue LED	1	$6.66	$6.66
Solvent Bottle (500 mL)	3	$21.58	$7.19
Plasti Dip Spray, Black	5	$5.82	$1.16
X-Acto Knife	20	$5.90	$0.29
Electrical Tape, Black	20	$4.48	$0.22
	Total	$70.65	$31.29

Description of items and where each was purchased online:

Heatsink:

Aluminum heatsink with an overall size of 50 mm x 50 mm x 20 mm. Larger heatsinks or copper heatsinks will work as well.

https://www.amazon.com/gp/product/B010ESEB8E/ref=oh_aui_detailpage_o02_s00?ie=UTF8&psc=1

Power Adapter:

AC to 9 V 300mA DC power adapter. The LED is rated for 8-10 V with a max current of 1050 mA. Using the LED at a higher current or voltage will require a larger heatsink and possibly a fan.

120 V AC:

https://www.amazon.com/gp/product/B00191WVF6/ref=oh_aui_detailpage_o02_s01?ie=UTF8&psc=1

220V AC:

https://www.amazon.com/Super-Power-Supply%C2%AE-compatible-Tru-Strobe/dp/B00HM7WWZA

Thermal Adhesive:

A permanent thermal adhesive that will bind the LED to the heatsink while still allowing for heat flow. To activate the adhesive, mix syringe A and B in a 50/50 volume ratio. Once thoroughly mixed, use immediately. DO NOT USE REGULAR GLUE OR A THERMAL GREASE.

https://www.amazon.com/gp/product/B0087X7262/ref=oh_aui_detailpage_o01_s01?ie=UTF8&psc=1

Alligator Clips to Female DC Jack:

Converts the male jack from the power adapter to positive and negative alligator clips that will be connected to the LED.

http://www.ebay.com/itm/321781825340?_trksid=p2057872.m2749.l2649&ssPageName=STRK%3AMEBIDX%3AIT

Blue LED:

A 10 W Royal Blue LED that emits in the range of 440-450 nm. The forward voltage range is from 8-10 V with a max forward current at 1050 mA. Do not use a power adaptor that is higher than the recommended range.

http://www.ebay.com/itm/131345637382?_trksid=p2057872.m2749.l2649&var=430695065092&ssPageName=STRK%3AMEBIDX%3AIT

Acetone Lab Solvent Bottle:

Standard 500 mL solvent bottle. Any plastic bottle will work as long as it will fit both the LED chip and the alligator clips.

https://us.vwr.com/store/product/12054719/scienceware-2-color-wash-bottles-safety-vented-and-safety-labeled-wide-mouth-bel-art

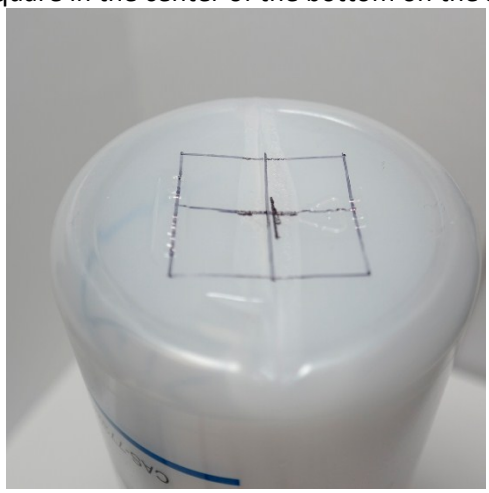
Plasti Dip Spray, Black:

Plasti Dip applies a rubber coating that is resistant to chemicals and abrasion. Spray paint will also work as long as it is black and suitable for plastic.

https://www.walmart.com/ip/Plasti-Dip-Spray-Black-11203-6/21015329

Photoreactor Construction Instructions:

1. Mark a 3.25 cm x 3.25 cm square in the center of the bottom on the solvent bottle.

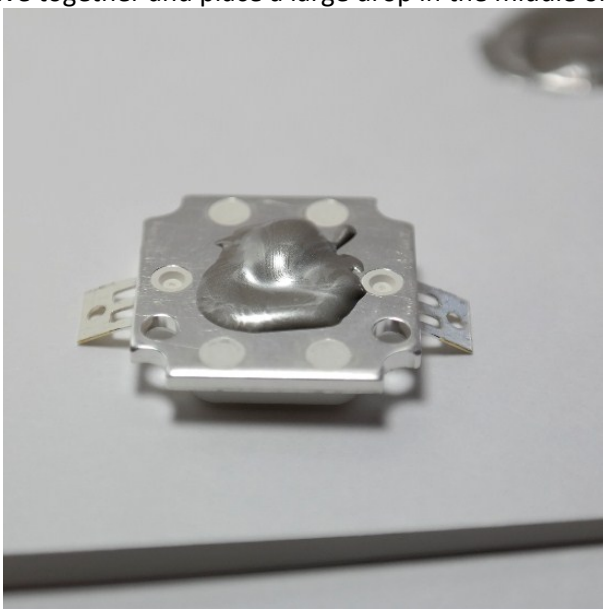


2. Cut out the square using an x-acto knife.

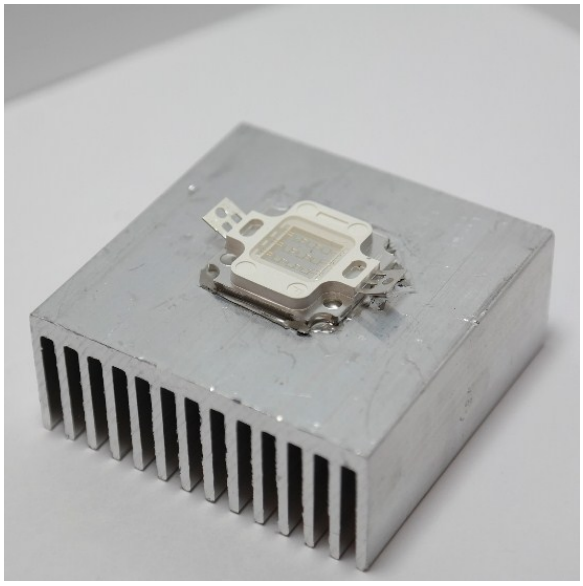
3. Cut a cross with the x-acto knife that is 2 cm x 2 cm with the center being 3cm from the bottom.

4. Paint the bottle black using Plasti Dip. Make sure to apply several layers to minimize the amount of light that shines through the bottle. Shine a flashlight through the bottle to make sure enough coats are applied.

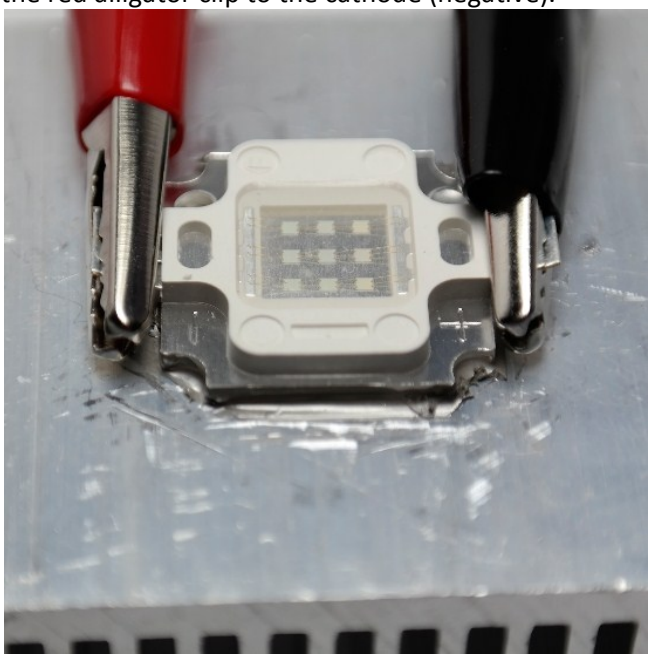
5. Mix the thermal adhesive together and place a large drop in the middle on the back of the LED.



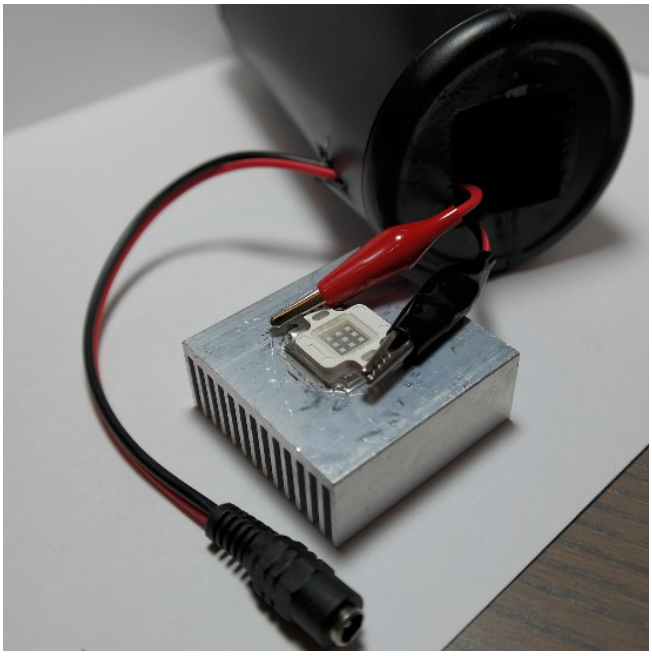
6. Place the LED in the middle of the heatsink and apply light pressure. The thermal adhesive should ooze out from the LED. Let cure for 15 min. Remove excess adhesive surrounding the LED with the x-acto knife.



7. Locate the positive and negative signs on the top of the LED. Attach the black alligator clip to the anode (positive) and the red alligator clip to the cathode (negative).



8. Place the bottle over the LED and alligator clips. Feed the DC female jack through the cross that was cut in the bottle in step 3.



9. Tape the heatsink to the bottle using black electrical tape. Also apply electrical tape over the cross and the DC female jack.

10. Plug in the DC female jack into the male AC/DC power supply. The photoreactor is now complete.

Figure S1: *n*-Butyl Acrylate Pseudo-First Order Kinetics

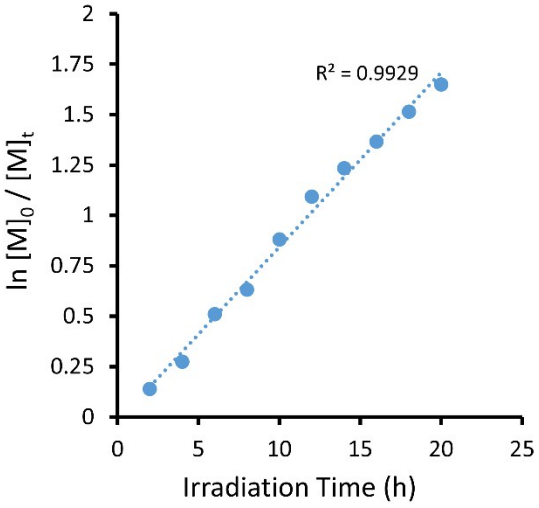


Table S2: Kinetics Data for Photoiniferter Polymerization of nBA

Time (h)	Conversion[A]	M_n (kDa)[B]	Đ[B]
2	0.13	1.2	1.005
4	0.24	2.1	1.001
6	0.40	3.3	1.004
8	0.47	4.3	1.002
10	0.59	5.3	1.004
12	0.66	6.0	1.003
14	0.71	6.4	1.001
16	0.74	6.7	1.005
18	0.78	7.1	1.001
20	0.81	7.4	1.004

[A]Determined by ^{1}H NMR spectroscopy in $CDCl_3$ by comparing integrations of the monomer vinyl peaks to polymer backbone peaks. [B]M_n and Đ values were measured by SEC in THF at 30 °C using refractive index and light scattering detectors.

Figure S2: ACMO Pseudo-First Order Kinetics

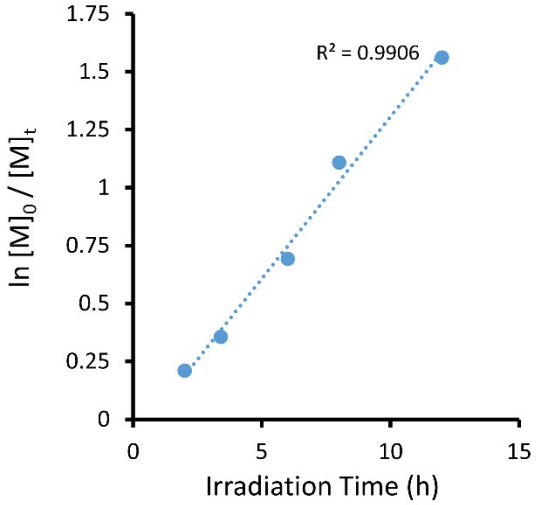


Table S3: Kinetics Data for Photoiniferter Polymerization of ACMO

Time (h)	Conversion[A]	M_n (kDa)[B]	Đ[B]
2	0.19	1.2	1.01
4	0.38	4.4	1.04
6	0.50	8.3	1.01
8	0.67	12	1.02
12	0.79	15	1.02

[A]Determined by ^{1}H NMR spectroscopy in $CDCl_3$ by comparing integrations of the monomer vinyl peaks to polymer backbone peaks. [B]M_n and Đ values were measured by SEC in THF at 30 °C using refractive index and light scattering detectors.

Figure S3: Styrene Pseudo-First Order Kinetics

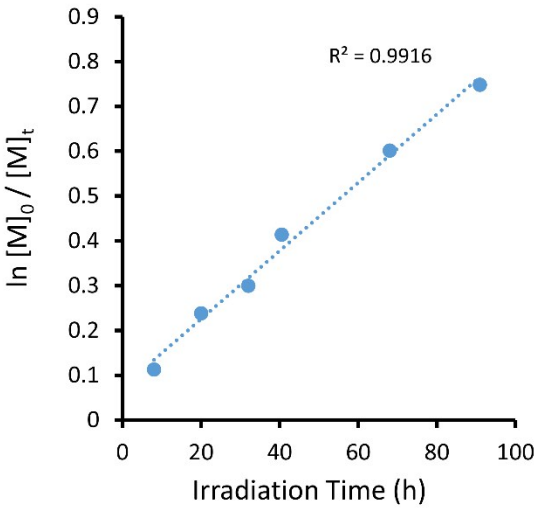


Table S4: Kinetics Data for Photoiniferter Polymerization of Styrene

Time (h)	Conversion[A]	M_n (kDa)[B]	Đ[B]
10	0.15	0.93	1.02
20	0.21	1.7	1.05
30	0.25	3.0	1.05
40	0.33	4.0	1.05
70	0.45	7.0	1.09
90	0.53	7.6	1.18

[A]Determined by ^{1}H NMR spectroscopy in $CDCl_3$ by comparing integrations of the monomer vinyl peaks to polymer backbone peaks. [B]M_n and Đ values were measured by SEC in THF at 30 °C using refractive index and light scattering detectors.

References

1. S. C. Radzinski, J. C. Foster, R. C. Chapleski Jr, D. Troya and J. B. Matson, *J. Am. Chem. Soc*, 2016, **138**, 6998-7004.