SI-PET-RAFT: Surface-Initiated Photo-Induced Electron Transfer-Reversible Addition–Fragmentation Chain Transfer Polymerization

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General material information

Styrene, *N,N*-dimethylacrylamide (DMA), methyl methacrylate (MMA), poly(ethylene glycol) methyl ether methacrylate (PEGMA), 2,2,2-trifluoroethyl methacrylate (TFEMA), 4-cyano-4-(phenylcarbonothioylthio) pentanoic acid (CPADB), 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT), (3-aminopropyl) triethoxysilane (APTES), *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (EDC HCl), zinc

tetraphenylporphyrin (ZnTPP), tris(2-phenylpyridine)iridium(III) (*fac*-Ir(ppy)₃]), 2,2 ′ -azobis(2-methylpropionitrile) (AIBN), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and ethyl acetate were purchased from Sigma-Aldrich and used as received (unless otherwise noted).

Methylene dichloride (DCM), toluene, isopropanol, and hexanes were purchased from Fisher Scientific and used as received. Methacrylic acid *N*-hydroxysuccinimide ester (NHSMA) was synthesized following a previously reported procedure.[1] Silicon wafers with native oxide and 100 nm thermal oxide layers were purchased from WaferPro, LLC (San Jose, CA). A striped photomask was purchased from Photronics, Inc (Brookfield, CT). Grayscale photomasks were printed by Fineline Imaging (Colorado Springs, CO). Thorlabs Olympus BX & IX series (λ = 365 and 405 nm) collimated light-emitting diodes (LEDs) were used for all light-mediated reactions (unless otherwise noted). LED light intensities were modulated by a Thorlabs LED D1B T-cube driver. All the other projector parts, including posts, holders, and lenses were also obtained from Thorlabs.

General analytical information

Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker AVIII-HD-500 MHz instrument. All ¹H NMR experiments are reported in δ units, parts per million (ppm), and were normalized to the signal for the deuterated solvent CDCl₃ (7.26 ppm). X-ray photoelectron spectroscopy (XPS) measurements were performed using a Physical Electronics PHI VersaProbe II Spectrometer with a monochromatic Aluminum K_α X-ray source (1486.6 eV) under a vacuum of 10^{-8} Torr. Spectra were analyzed using CasaXPS software (Casa Software Ltd.). Atomic Force Microscopy (AFM) was performed using Bruker Dimension Icon with ScanAsyst® scan mode. The measurement was conducted using a silicon nitride cantilever with a silicon tip. Optical micrographs of polymer brush patterns were captured using Carl Zeiss Axio Scope A1 equipped with Axiocam 305 color camera. Film thickness was measured using a J.A. Woollam RC2-D variable-angle spectroscopic ellipsometer (VASE) at 55°, 65°, and 75° incident angles and a wavelength range from 193 to 1000 nm. The CompleteEASE software package (J.A. Woollam Co., Inc.) was used for fitting the optical constants and thicknesses. Unless otherwise noted, three-layer models containing (a) a silicon substrate layer at the bottom, followed by (b) a 1.55-nm-thick native silicon oxide layer and then (c) a polymer film layer were used. Thicknesses and optical constants of polymer film layers were fitted using Gen-Osc models containing several Gaussian generalized oscillators. (See **Figure S10**)

Synthetic procedures for DDMAT- and CPADB-derived surface RAFT CTA

### Synthesis of DDMAT-derived surface RAFT CTA (Compound 2)
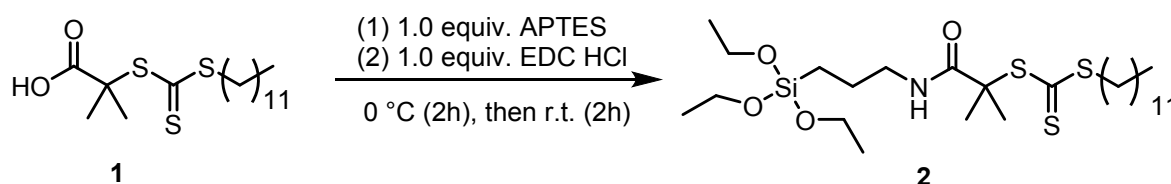
A 250 mL flask equipped with a magnetic stir bar and rubber septum was charged with 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) (**1**, 364.6 mg, 1 mmol) and DCM (50 mL). *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC HCl) (191.7 mg, 1 mmol) dissolved in DCM (10 mL) was then added dropwise into the flask. The solution was then cooled and stirred at 0 °C for 10 min. Sequentially, (3-aminopropyl) triethoxysilane (APTES) (0.23 mL, 1 mmol) was added dropwise into the solution. The reaction mixture was stirred at 0 °C for 2 hours, then at room temperature for 2 hours, and then concentrated in vacuo. The crude product was purified with silica gel column chromatography (1:1 v/v ethyl acetate and hexanes) to provide the title compound **2** as a viscous yellow liquid. ¹H NMR (500 MHz, CDCl₃, 25 °C, δ, ppm): 0.59 (s, 2H), 0.88 (t, 3H), 1.22 (t, 9H), 1.30 (m, 18H), 1.58 (m, 2H), 1.66 (m, 2H), 1.69 (s, 6H), 3.22 (q, 2H), 3.27 (t, 2H), 3.81 (q, 6H), 6.62 (t, 1H) (see **Figure S1**)
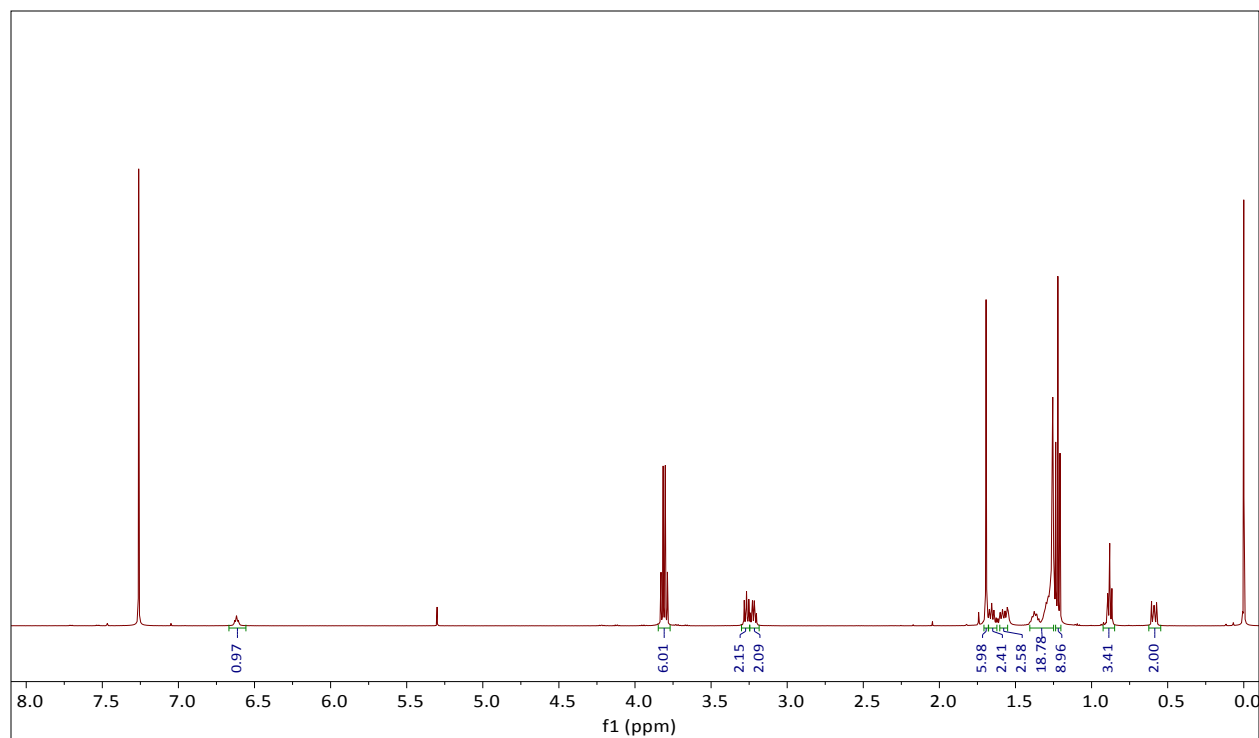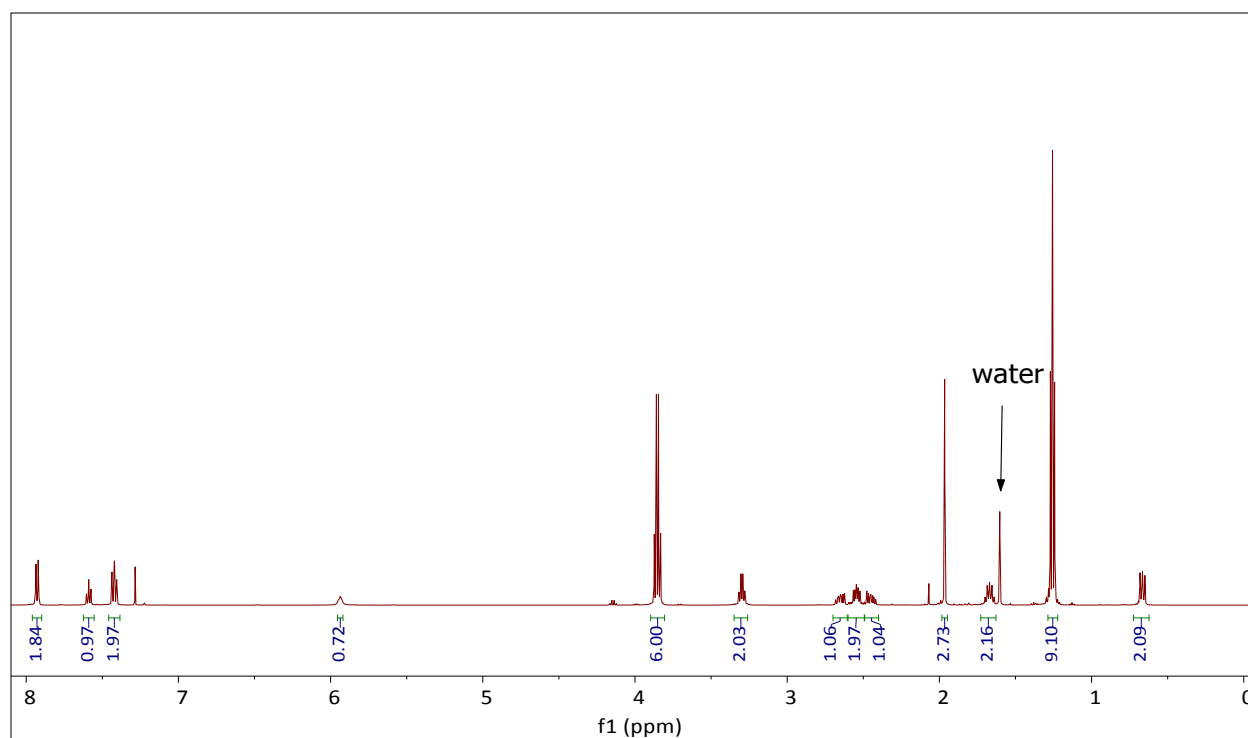
Figure S1. NMR spectrum of DDMAT-derived RAFT CTA (compound **2**)

## Synthesis of CPADB-derived RAFT CTA (Compound 4)
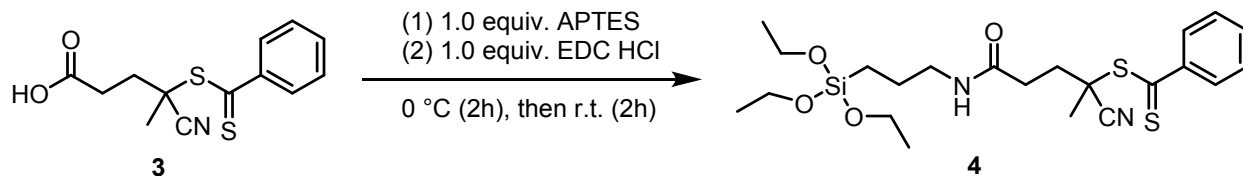
A 250 mL flask equipped with a magnetic stir bar and rubber septum was charged with 4-cyano-4-(phenylcarbonothioylthio) pentanoic acid (CPADB), (**3**, 279.4 mg, 1 mmol) and DCM (50 mL). EDC HCl (191.7 mg, 1 mmol) dissolved in DCM (10 mL) was then added dropwise into the flask. The solution was then cooled and stirred at 0 °C for 10 min (to ensure deprotonation of DDMAT). Sequentially, APTES (0.23 mL, 1 mmol) was added dropwise into the solution. The reaction mixture was stirred at 0 °C for 2 hours, then at room temperature for 2 hours, and then concentrated in vacuo. The crude product was purified with silica gel column chromatography (1:1 v/v ethyl acetate and hexanes) to provide the title compound **4** as a viscous pink liquid. ^{1}H NMR (500 MHz, CDCl$_3$, 25°C, δ, ppm): 0.67 (m, 2H), 1.22 (t, 9H), 1.67 (m, 2H), 1.97 (s, 3H), 2.44 (m, 1H), 2.54 (m, 2H), 2.65 (m, 1H), 3.29 (q, 2H), 3.85 (q, 6H), 5.94 (s, 1H), 7.42 (t, 2H), 7.59 (m, 1H), 7.93 (d, 2H) (see **Figure S2**)

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Figure S2. NMR spectrum of CPADB-derived RAFT CTA (compound **4**)

RAFT CTA functionalized surface
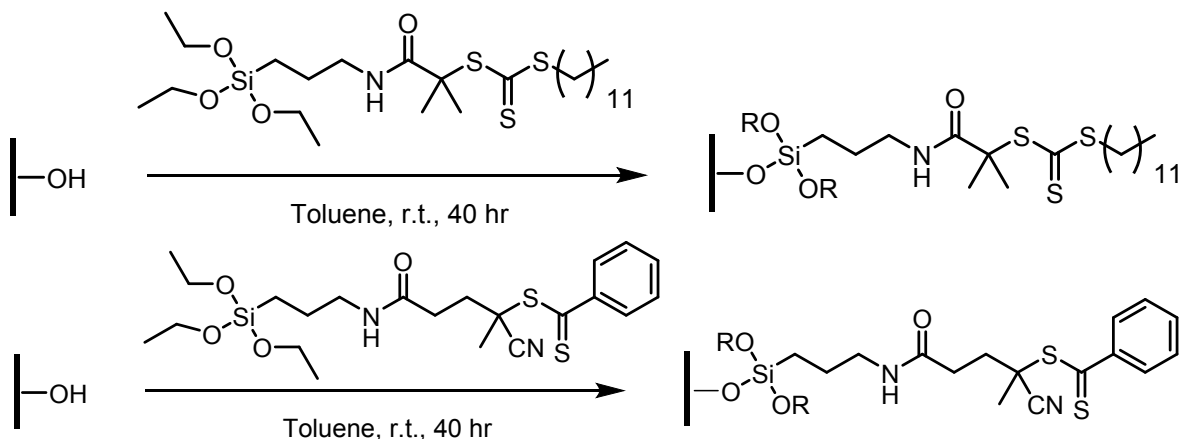
Silicon substrates with a layer of native oxide were cut into 1 cm × 1 cm squares, cleaned by sonication in toluene followed by isopropanol, and then dried under a stream of nitrogen gas. The wafers were then cleaned and activated by a plasma cleaner (PDC-001, Harrick Plasma) under 300 mTorr of air for 10 min. After cleaning, the wafers were placed in a dilute solution containing 125 µL of synthesized RAFT CTA (compound **2** or **4**) in 250 mL of dry toluene (0.05% v/v) for 40 hours. Upon completion, the functionalized substrates were rinsed thoroughly with toluene followed by isopropanol, dried under a stream of nitrogen gas, and then stored under nitrogen. XPS spectra confirmed successful functionalization of RAFT CTAs (see **Figure S3**), with peaks from the substrate (BE_{Si2s} = 149 eV and BE_{Si2p} = 99 eV) supplemented by carbon (BE_{C1s} = 285 eV), nitrogen (BE_{N1s} = 400 eV) and oxygen (BE_{O1s} = 532 eV) peaks from compounds 2 or 4, respectively.

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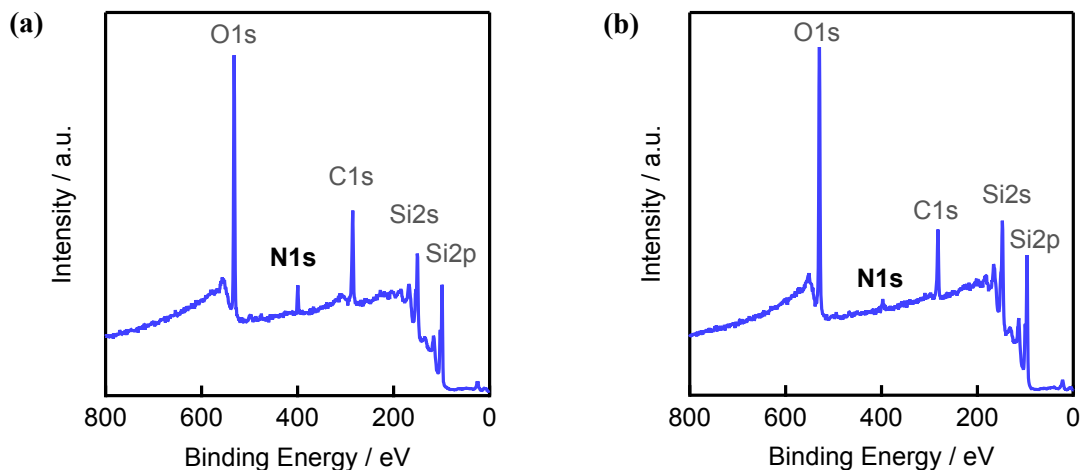
Figure S3. (a) XPS survey spectra for DDMAT- and (b) CPADB-derived RAFT CTA functionalized surfaces. The presence of N1s peaks (400 eV) from the anchoring group confirmed successful attachment.

General procedures for SI-PET-RAFT

Unless otherwise noted, all reactions were placed approximately 1.5 cm below an LED light source both in glovebox and fume hood setups. A stock solution containing 1 mg of photocatalyst (ZnTPP or Ir(ppy)$_3$) in 1 mL DMSO was prepared in a vial and stored in the dark. Monomers were purified through a basic alumina column to remove inhibitor prior to use. The inhibitor-free monomers, RAFT CTA (DDMAT or CPADB), and the photocatalyst/DMSO stock solution were mixed in a 4 mL vial with a molar ratio of [Monomer]:[CTA]:[Photocat.] = 500:1:0.025 (unless otherwise noted) to form the reaction mixture. A CTA-functionalized silicon wafer was placed on top of a glass slide and the reaction mixture was then pipetted onto the wafer until completely covered. A glass coverslip was then placed on top of the wafer to form a thin layer of solution in between the coverslip and wafer. Unless otherwise noted, each sample was irradiated with $\lambda = 405$ nm light at an intensity of 1.1 µW/cm^2 for a desired amount of time. After irradiation, the wafers were thoroughly rinsed with DCM (unless otherwise noted) followed by isopropanol, and then dried under a stream of nitrogen gas. For reactions under inert gas, the reaction mixture was sparged for 5 min before the reaction was performed in a glovebox under nitrogen atmosphere. For reactions exposed to air, the reaction mixture was used directly for the reaction inside the fume hood.

General procedures for thermal SI-RAFT

Styrene was purified through a basic alumina column to remove inhibitor prior to use. Inhibitor-free styrene (2.4 mL, 20 mmol) was then mixed with DDMAT (19.1 mg, 0.05 mmol) and 2,2′-azobis(2-methylpropionitrile) (AIBN) (1.7 mg, 0.01 mmol) to form a reaction mixture with a molar ratio of [styrene]:[DDMAT]:[AIBN] = 400:1:0.2. The reaction mixture was then transferred into a 20 mL vial with a functionalized wafer, sparged with nitrogen for 5 min and then heated at 85 °C for 1 hour. Upon completion, the reaction was quenched by placing the reaction vial into an ice bath for 10 min. The wafer was then thoroughly rinsed with toluene followed by isopropanol and then dried under a stream of nitrogen gas.

Control experiment without photocatalysts

DMA was purified through a basic alumina column to remove inhibitor prior to use. The inhibitor-free DMA (515 µL, 5 mmol), DDMAT (3.6 mg, 0.01 mmol), and DMSO (170 µL) were mixed in a 4 mL vial to form the reaction mixture with a molar ratio of [Monomer]:[CTA]:[Photocat.] = 500:1:0. The reaction mixture was sparged with nitrogen for 5 min and then transferred into a glovebox under nitrogen atmosphere. In the glovebox, a DDMAT-functionalized silicon wafer was placed on top of a glass slide and the reaction mixture was then pipetted onto the wafer until completely covered. A glass coverslip was then placed on top of the wafer to form a thin layer of solution between the coverslip and wafer. After irradiation with $\lambda = 405$ nm light at an intensity of 1.1 µW/cm^2 for 1 h, the wafers were thoroughly rinsed with DCM followed by isopropanol, and then dried under a stream of nitrogen gas.

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The film thickness was then measured via ellipsometry, and no thickness increase was observed within error after the reaction. XPS spectra of the sample matched DDMAT-functionalized substrates before the reaction (See **Figure S4** and **Table S1**).
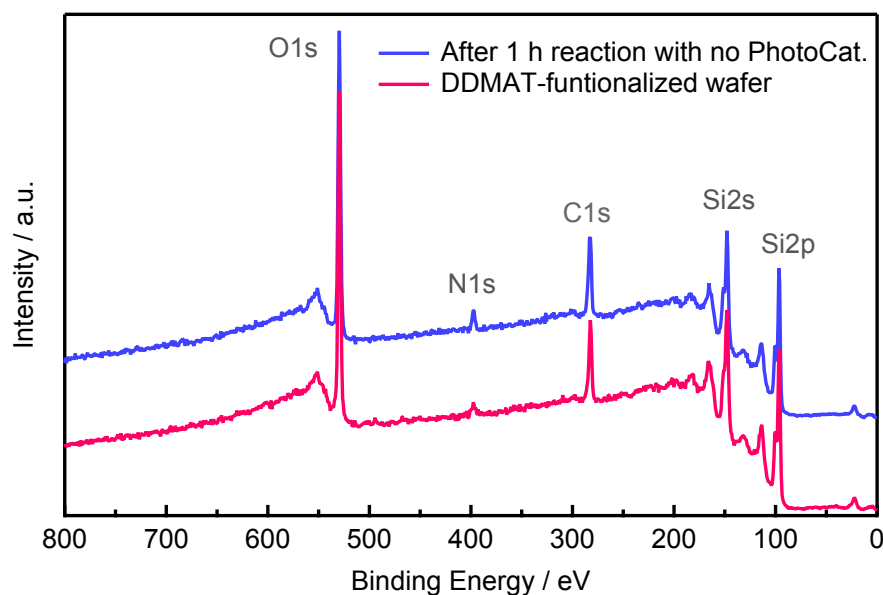

Figure S4. XPS survey scan spectra of the sample before (bottom, magenta) and after (top, blue) the control experiment. Strong Silica Si_{2s} and Si_{2p} signals and a negligible increase in other peaks after reaction indicate no noticeable polymer brush layer on the functionalized silicon substrate.

Table S1. Binding energies and atomic percentages before and after reaction (corresponding to Figure S4)

| Component	BE (eV)	At.% (before)	At.% (after)
C1s	285	21.44	24.26
N1s	400	1.61	3.64
O1s	532	33.45	32.57
Si2s	149	43.50	39.53
Si2p	99	43.50	39.53

Control experiments without 'free' RAFT CTA

Polymerization of DMA was performed under optimized conditions (50 ppm ZnTPP) but without the addition of 'free' RAFT chain-transfer agent in the reaction mixture (see **Figure S5**). Polymer brush thickness, d, increases rapidly and plateaus off at around $d = 110$ nm. To probe for the fidelity of the chain ends, we attempted to chain extend some of the polymer brush wafers. These extension attempts were unsuccessful and, within measurement error, the polymer brush films showed no increased thickness. In **Figure S5**, filled and empty circles represent the thickness of the initial brush layer and the thickness after attempted chain extension, respectively. The difference on the x-axis (Δt in minutes) between empty and filled circles is indicative of the amount of time the second polymerization attempt was run for before cleaning the substrate and measuring the final film thickness. As discussed in greater detail in the main manuscript, these findings suggest an uncontrolled, free radical polymerization process.
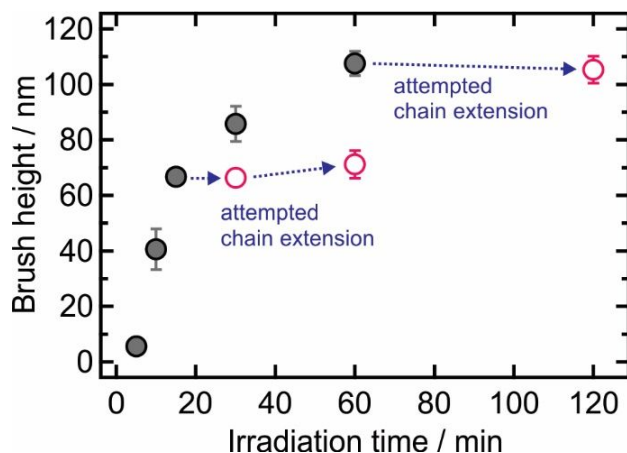
Figure S5. SI-PET-RAFT of p(DMA) in the absence of free RAFT chain-transfer agent. Dark circles represent kinetics data of SI-PET-RAFT being performed for the indicated time. Empty circles represent failed attempts at extending the initially grown p(DMA) polymer brushes.

SI-PET-RAFT Polymerization of Butyl Acrylate

Using the optimized conditions described in the manuscript ([BA]:[DDMAT]:[ZnTPP] = 500:1:0.025) and a 5 micron striped photomask, we were able to use SI-PET-RAFT to pattern poly(butyl acrylate) polymer brushes (see **Figure S6**).
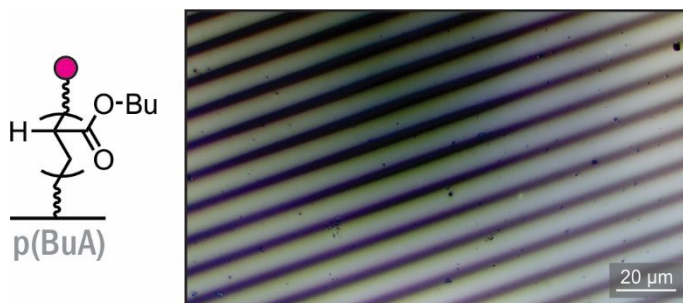
Figure S6. Optical micrograph of patterned poly(butyl acrylate) polymer brushes.

XPS and micrographs of monomer tolerance

A stock solution containing 1 mg of photocatalyst $Ir(ppy)_3$ in 1 mL DMSO was prepared in a vial and stored in the dark. Monomers were purified through a basic alumina column to remove inhibitor prior to use. The inhibitor-free monomers, CPADB, and the $Ir(ppy)_3$/DMSO stock solution were mixed in a 4 mL vial with a molar ratio of [Monomer]:[CTA]:[Photocat.] = 500:1:0.025 to form the reaction mixture. The reaction mixture was sparged with nitrogen for 5 min and then transferred into a glovebox under nitrogen atmosphere. In the glovebox, a CPADB-functionalized silicon wafer was placed on top of a glass slide and the reaction mixture was then pipetted onto the wafer until completely covered. A striped binary photomask was then placed on top of the wafer to form a thin layer of solution in between the photomask and wafer. Each sample was irradiated with $\lambda = 405$ nm light at an intensity of 1.1 $\mu W/cm^2$ overnight. After irradiation, the wafers were thoroughly rinsed with DCM (or DMF for pNHSMA) followed by isopropanol, and then dried under a stream of nitrogen gas. Patterns on the wafer were then captured with an optical microscope. Successful growths of polymer brushes were confirmed by XPS and optical microscopy (see **Figure S7** and **Table S2**).
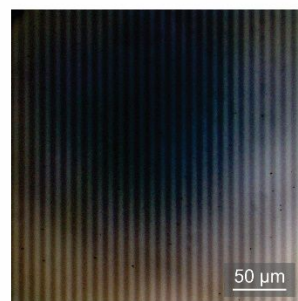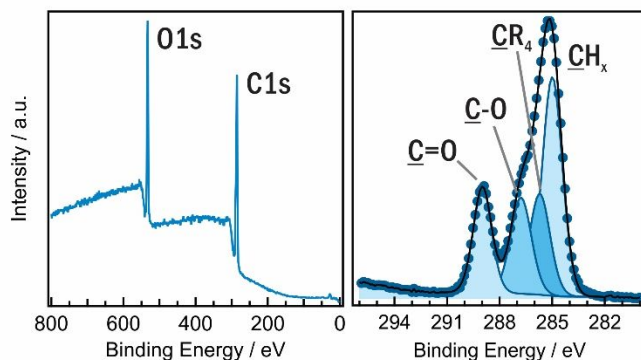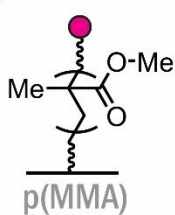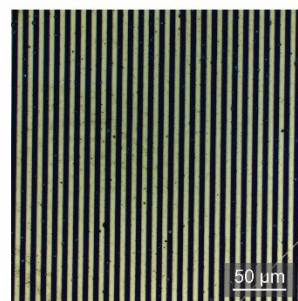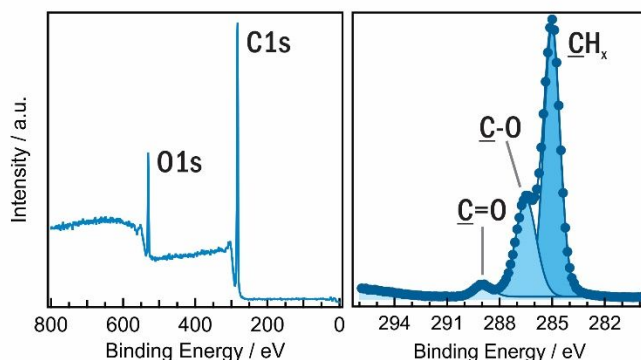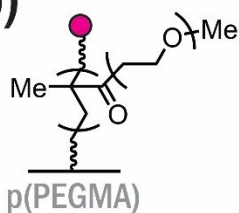
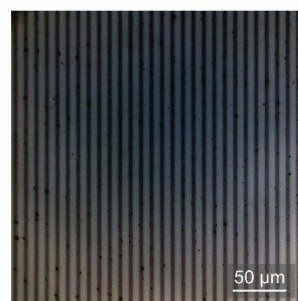| Chem. Structure	XPS Survey & High-Resolution C1s	Optical Micrograph

(a) p(MMA)

(b) p(PEGMA)
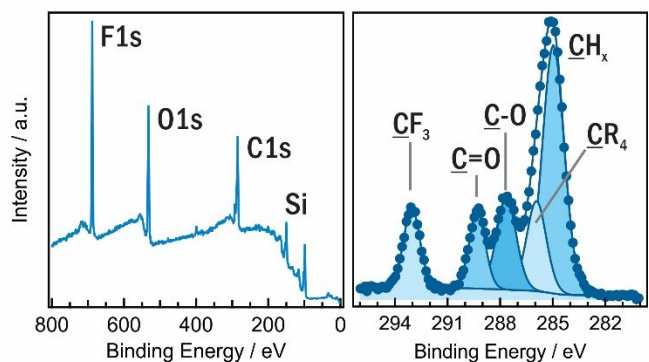
(c) p(TFEMA)

(d) p(NHSMA)
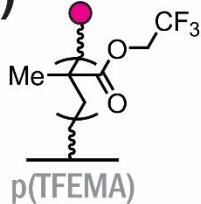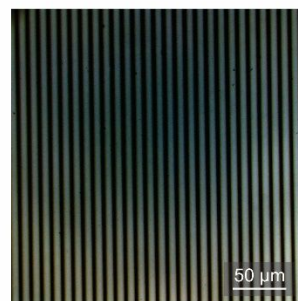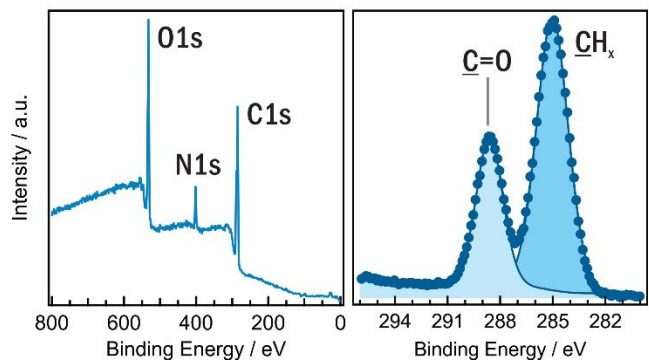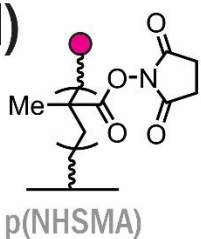
Figure S7. X-ray Photoelectron Spectroscopy (XPS) survey and high-resolution carbon C1s spectra for patterned (a) p(MMA), (b) p(PEGMA), (c) pTFEMA and (d) pNHSMA polymer brushes.

**Table S2.** XPS peak positions for high-resolution C1s spectra in Figure S7.

	p(MMA)			p(TFEMA)		
	BE (eV)	At.%	ratio	BE (eV)	At.%	ratio
CH	285.0	42.1	2	285.0	46.8	2
CR	285.7	20.0	1	285.9	15.5	1
C-O	286.8	19.2	1	287.6	15.7	1
C=O	289.0	18.7	1	289.3	10.7	1
C-F	-	-	-	293.0	11.3	1

|	p(PEGMA)			p(NHSMA)		
	BE (eV)	At.%	ratio	BE (eV)	At.%	ratio
CH	285.0	68.0	-	285.0	68.7	5
C-O	286.5	29.2	-	288.6	31.4	3
C=O	289.0	2.8	-			

Cross-patterned micrographs via chain extension

A stock solution containing 1 mg of ZnTPP in 1 mL DMSO was prepared in a vial and stored in the dark. DMA was purified through a basic alumina column to remove inhibitor prior to use. The inhibitor-free DMA (412 μL, 4 mmol), DDMAT (7.3 mg, 0.02 mmol), and the ZnTPP/DMSO stock solution (136 μL) were mixed in a 4 mL vial to form the reaction mixture with a molar ratio of [Monomer]:[free CTA]:[Photocat.] = 200:1:0.01. For the initial stripe-patterned layer, a DDMAT-functionalized silicon wafer was placed on top of a glass slide and the reaction mixture was then pipetted onto the wafer until completely covered. A striped binary photomask was then placed on top of the wafer to form a thin layer of solution between the photomask and wafer. Each sample was irradiated with a 26-watt white compact fluorescent lamp for 2 hours. After irradiation, the wafers were thoroughly rinsed with DCM followed by isopropanol, and then dried under a stream of nitrogen gas in the dark. To obtain the cross-patterned second layer, the same reaction was performed on the initial stripe-patterned wafer by placing the photomask orthogonally as shown in **Figure S8** (a, b). For reactions under inert gas, the reaction mixture was sparged for 5 min before the reaction was performed in a glovebox under nitrogen atmosphere. For reaction exposed to air, the reaction mixture was used directly for the reaction in fume hood. Patterns on the wafers were captured after each SI-PET-RAFT with an optical microscope.
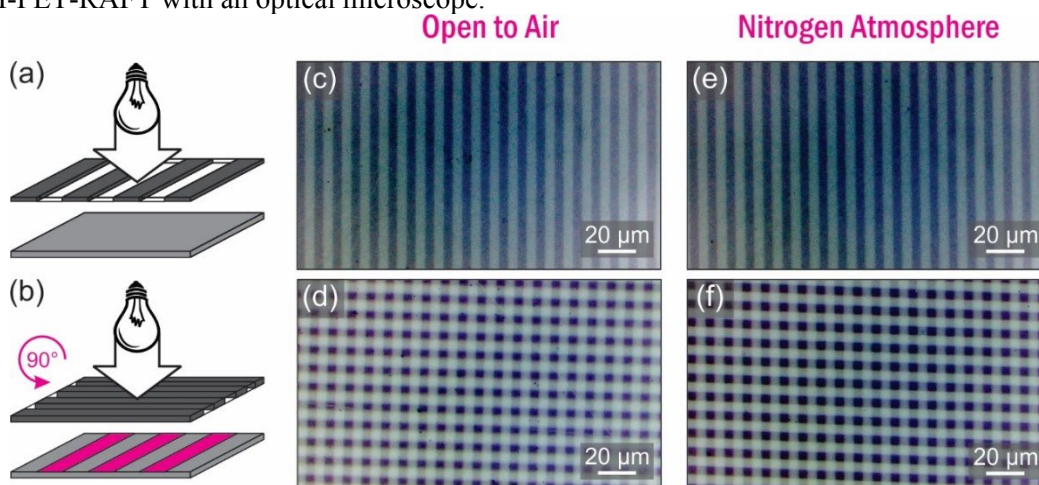
Figure S8. Sequential patterning of orthogonal stripes via SI-PET-RAFT. (a, b) Schematics of cross-patterning setup. Optical micrographs of initial stripe-patterned layer formed (c) in the presence of air and (e) under nitrogen atmosphere, and cross-patterned diblock copolymers formed (d) in the presence of air and (f) under nitrogen atmosphere.

Reduction lithography patterning

A stock solution containing 1 mg of ZnTPP in 1 mL DMSO was prepared in a vial and stored in the dark. DMA was purified through a basic alumina column to remove inhibitor prior to use. The inhibitor-free DMA (2.1 mL, 20 mmol), DDMAT (14.6 mg, 0.04 mmol), and the ZnTPP/DMSO stock solution (0.678 mL) were mixed in a 4 mL vial to form the reaction mixture with a molar ratio of [Monomer]:[free CTA]:[Photocat.] = 500:1:0.025. Using a similar setup as reported in the previous literature[2], a DDMAT-functionalized silicon wafer was placed in a cell under the reduction lithography projector (see **Figure S9**). The reaction mixture was injected into the cell after short 2min sparging via cannula transfer and then irradiated with $\lambda = 405$ nm light for 1 hour. After irradiation, the wafer was thoroughly rinsed with DCM followed by isopropanol, and then dried under a stream of nitrogen gas. The micrograph on the wafer was then captured with an optical microscope. Atomic force microscopy (AFM) was used to confirm topographical patterning.
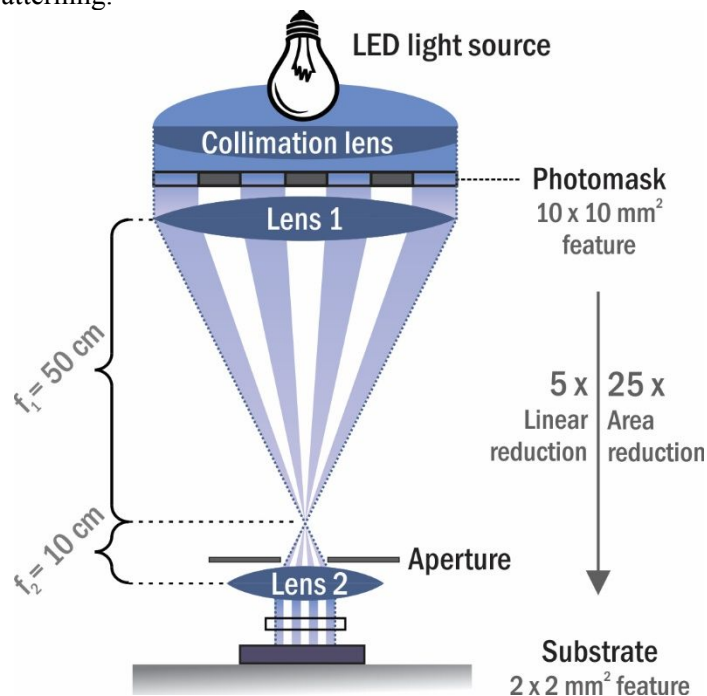
Figure S9. Schematic of reduction lithography. An array of lenses is used to project the pattern of a photomask onto a CTA-functionalized substrate. Using focal lengths of $f_1 = 50$ cm and $f_2 = 10$ cm, the features of the original photomask image were reproduced on the surface with a linear reduction of LRF = f_1/f_2 = 5, equaling a 25x reduction in area.

Example of ellipsometry models and measurements

A three-layer model containing (a) a silicon substrate layer at the bottom, followed by (b) a 1.55-nm-thick native silicon oxide layer and then (c) a pDMA brush layer was used. The thickness and optical constants of polymer film layers were fitted using Gen-Osc models containing two Gaussian generalized oscillators. Example values for the fit of a pDMA brush are shown in **Figure S10**.
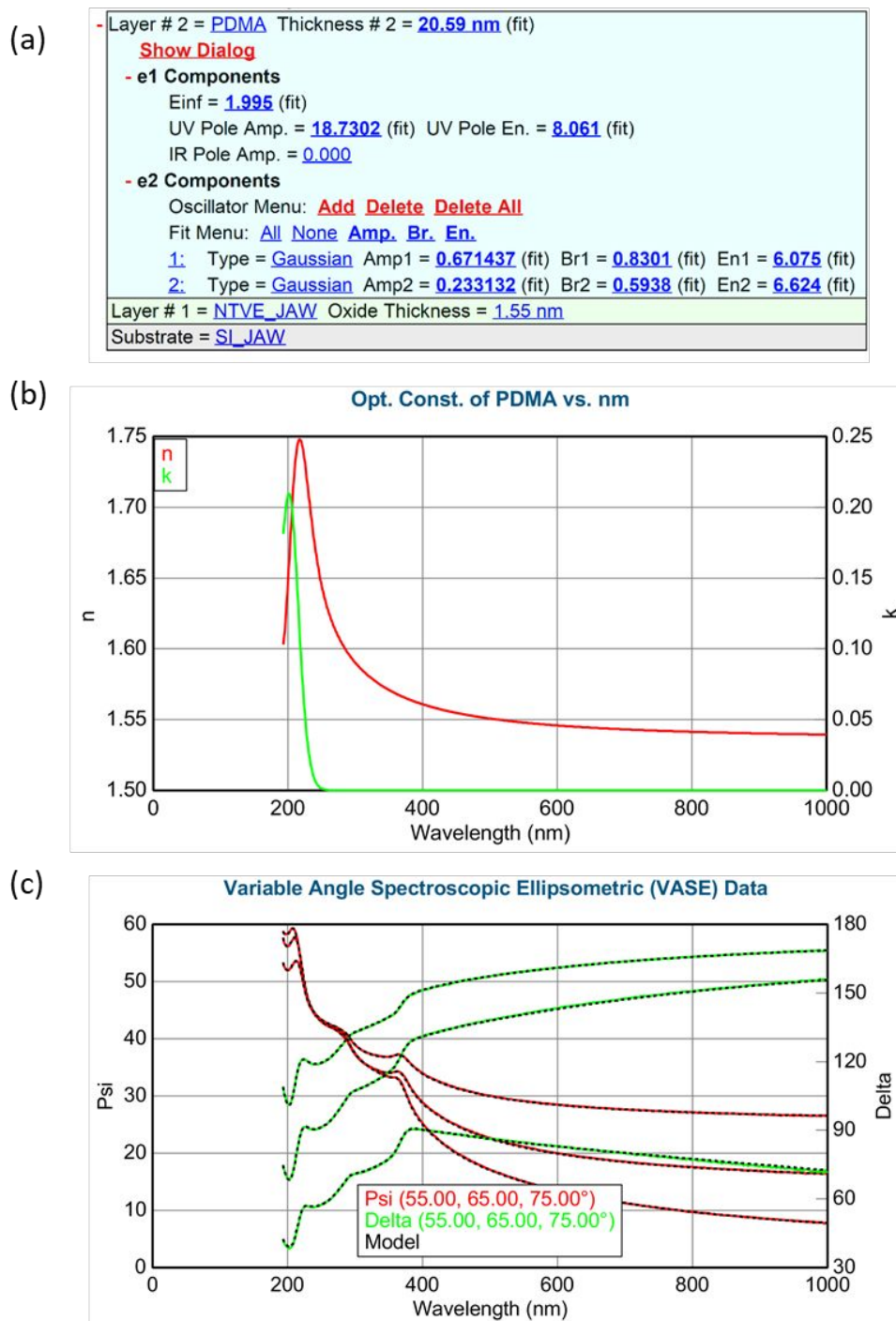
Figure S10. Ellipsometry measurement on a pDMA polymer brush using (a) three-layer model. (b) Optical constants, *n* and *k*, were fitted by a Gen-Osc model with two Gaussian generalized oscillators. (c) Measured Ψ (red solid line) and Δ (green solid line) were well-fitted by the three-layer model (black dashed line).

References

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(2)   Pester, C. W.; Narupai, B.; Mattson, K. M.; Bothman, D. P.; Klinger, D.; Lee, K. W.; Discekici, E. H.; Hawker, C. J. Engineering Surfaces through Sequential Stop-Flow Photopatterning. *Adv. Mater.* **2016**, *28*, 9292-9300.