Supporting Information

Hydrolysis-Resistant Heterogeneous Photocatalysts for PET-RAFT Polymerization in Aqueous Environments

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General Material and Reagent Information

(3-Aminopropyl)triethoxysilane (APTES), fluorescein *o*-acrylate (FlA), *N*-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC HCl), 2,2'-azobis(2-methylpropionitrile) (AIBN), 30 w/w % hydrogen peroxide solution, methyl acrylate (MA), 4-Cyano-4-(phenylcarbonothioylthio)pentanoic acid (CPADB), 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT), poly(ethylene glycol)methyl ether acrylate (PEGMEMA), methyl methacrylate (MMA), 2-(dimethylamino)ethyl methacrylate (DMAEMA), [2-(methacryloyloxy)ethyl]trimethylammonium chloride solution (METAC), 2-methacryloyloxyethyl phosphorylcholine (MPC), [2-(methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide (SBMA), 3-sulfopropyl methacrylate potassium salt (SPMK), *N,N*-dimethylacetamide (DMA), *N*-Isopropylacrylamide (NIPAAm), sodium 4-vinylbenzenesulfonate (SVBS), lauroyl peroxide (LPO), fluorescein sodium salt, fluorescein free acid, hydrochloric acid (HCl), andsodium hydroxide (NaOH) were purchased through Sigma Aldrich. Ascorbic acid, 2-hydroxyethyl acrylate (HEA), and 2,2,2-trifluoroethyl methacrylate (TFEMA) were purchased through Fisher Scientific. All monomers containing inhibitor were passed through a basic alumina plug prior to use to remove the inhibitor. 4-Cyano-4-[dodecylsulfanylthiocarbonyl)sufanyl] pentanoic acid (CDTPA) was purchased through Boron Molecular. Sulfuric acid (98%) was purchased through VWR and used as received. Glass beads, acid-washed ≤106 μm and sand 50-70 mesh particle size were purchased through Sigma Aldrich and used as received. The anhydrous solvents dimethylformamide (DMF) was purchased through Sigma Aldrich and stored in a nitrogen atmosphere glovebox. The solvents toluene, dichloromethane (DCM), tetrahydrofuran (THF), hexane, dimethyl sulfoxide (DMSO), and methanol were used as received from Sigma Aldrich. The solvent ethanol was purchased through VWR and used as received. The solvent ethanol was purchased through VWR and used as received. Deionized water (DIW) used was from in house at the Pennsylvania State University's Chemical and Biomedical Engineering building. Silicon wafers with native oxide (1.55 nm) layer was purchased from WaferPro, LLC (San Jose, CA). Glass slides were purchased through Chemglass with a thickness of 1/8" and cut to desired size.

General Analytical Information

Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker AVIII-HD-500. All ^{1}H NMR experiments are reported in δ units, parts per million (ppm), and were normalized to the signal for deuterated solvent DMSO (2.5 ppm) or D_2O (4.79 ppm) unless otherwise noted.

X-ray photoelectron spectroscopy (XPS) for elemental analysis 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.).

Ultraviolet-visible spectroscopy (UV/vis) measurements were performed on Shimadzu UV-2600 spectrometer equipped with a standard detection module. Samples (100 μL) were diluted with 3 mL DIW and measured in a 3.5 mL quartz cuvette with a 10 mm path length (Sterna cells Inc). Transmittance was measured from 200 nm to 600 nm in 1 nm steps and absorbance calculated by referencing to pure DIW.

UV/vis Diffused Reflectance (DR) was performed on a Shimadzu UV-2600 with an ISR-2600 integrating sphere configured to the relative reflectance with respect to the reference Barium Sulfate and bare, unfunctionalized glass beads. The samples were made by loading into a powder cup with no dilution.

Water contact angle measurements were performed by using an in-house set-up and analyzed through ImageJ.

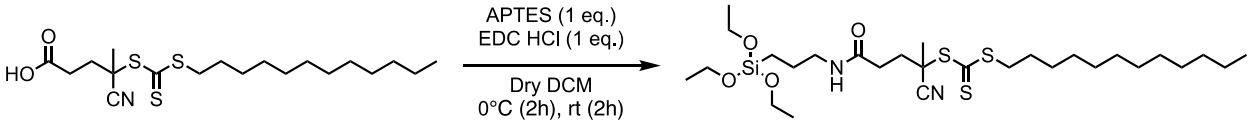
Film thickness were measured by using a J.A. Woollam RC2-D variable-angle spectroscopic ellipsometer (VASE) at 55°, 65°, and 75° incident angles and a wavelength of 400 to 1000 nm. The CompleteEASE software package (J.A. Woollam Co., Inc.) was used for fitting the optical constants and thicknesses. For the hydrophobic protective layer (Block 1, PTFEMA/PMMA) brush thickness a three-layer model containing (1) a silicon sub-strate layer at the bottom, followed (2) a 1.55-nm-thick native silicon oxide layer and then (3) a polymer film layer were used. For a diblock brush thickness, a four-layer model containing (1) a silicon substrate layer at the bottom, followed (2) a 1.55-nm-thick native silicon oxide layer and then (3) a polymer film layer (corresponds to the thickness of a monolayer prior the growth of second layer) and (4) a polymer film layer was used. For in situ swelling measurements, a 500 μL horizontal liquid cell with a window angle of 70° (J.A. Woollam Co., Inc.) was used. Upon injection of the solvent, the ellipsometer was aligned and started to collect data at 70°. When the equilibrium was achieved, i.e. the thickness fluctuated without a noticeable increasing or decreasing trend for at least 30 minutes, the average of fluctuated thicknesses was recorded. The D2 lamp (UV light source) was turned off and only QTH lamp (visible light source) was used to protect polymer brush films from decomposition under UV. Cauchy models were used to fit polymer brush layers using data collected under 400-1000 nm wavelengths. The optical constants of solvents (DIW) were determined on a non-swelling calibration wafer (25 nm SiO_2 on Si) in the 500 μL liquid cell. The thickness and optical constants of calibration wafer were known and the ambient (solvent) was fitted with a Cauchy model. For DIW, A= 1.324, B = 0.00311, C = -7.6185E-06 was used.

Sum frequency generation (SFG) spectroscopy measurements were carried out in both dry nitrogen and liquid water at the air/polymer and water/polymer interfaces using a scanning picosecond SFG spectrometer (EKSPLA, Lithuania). The SFG beam was generated by overlapping a visible (532 nm) laser beam from the picosecond laser and a tunable pulsed IR laser beam from an optical parametric generator and amplifier at a fixed frequency. The polarization combination used was ssp, with s- for the SFG signal beam, s- for the 532nm input visible beam, and p- for the tunable pulsed IR beam. The incident angles of the IR and visible beams were 56 and 60°, respectively, to the surface normal. A scanning step of 4 cm^{-1} in the range of 2800–3100 cm^{-1} and 14 cm^{-1} in the range of 3100–3800 cm^{-1} was used, with each data point being an average of 300 pulses. The SFG spectra were normalized to the intensity of input IR and visible lasers measured by detectors. The RH during the SFG measurements was controlled by mixing a dry nitrogen flow and a water vapor-saturated nitrogen flow at a given ratio. The measurements were carried out at room temperature (∼22 °C), and 0% RH in air or in water. The SFG plots were fitted using the nonlinear fitting model in Mathematica.

Gel Permeation Chromatography (GPC) was performed mostly on a Tosoh EcoSEC Elite GPC system with both Refractive Index (RI) and Ultraviolet (UV) detectors in tetrahydrofuran (THF) at 40°C with a flow rate of 1 mL min^{-1}. Number average molecular weights (M_N) and weight average molecular weights (M_W) were calculated relative to linear poly(methyl methacrylate) standards.

Surface Functionalization

General procedure for the synthesis of a RAFT CTA surface initiator



A 250 mL flask equipped with a magnetic stir bar and rubber septum was charged with 4-Cyano-4-[dodecylsulfanylthiocarbonyl)sufanyl] pentanoic acid (CDTPA, 403.7 mg, 1 mmol) and dry dichloromethane (DCM, 50 mL). *N*-(3-Dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC HCl) (191.7 mg, 1 mmol) dissolved in dry DCM (10 mL) was then added dropwise. The solution was cooled and stirred at 0°C for 10 min before APTES (0.23 mL, 1 mmol) was added dropwise. The reaction mixture was stirred at 0°C for 2 hours, then at room temperature for another 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 a viscous orange/yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 5.86 (s, 1H), 3.83 (q, 6H), 3.32 (t, 2H), 3.26 (q, 2H), 2.49 (m, 3H), 2.38 (m, 1H), 1.89 (s, 3H), 1.66 (m, 4H), 1.38 (m, 2H), 1.26 (m, 25H), 0.88 (t, 3H), 0.64 (m, 2H).

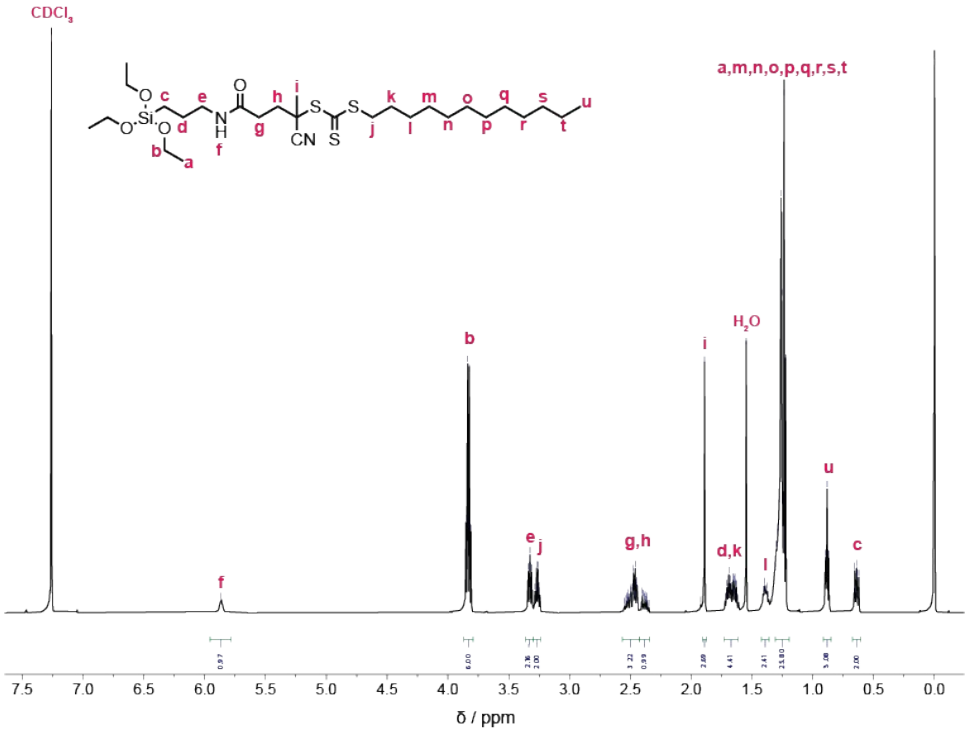


Figure SI. ^{1}H NMR spectrum of CDTPA-derived RAFT CTA surface initiator.

General procedure for the functionalization of planar substrates

Silicon wafers/glass slides were broken into pieces of ~1 cm × 1 cm and sonicated for 10 minutes in toluene followed by 10 minutes in isopropanol to remove any preexisting residues. They were then dried with a stream of nitrogen and arranged in a Petri dish, avoiding overlap. In the uncovered Petri dish, substrates were treated with an air plasma cleaner (PDC-001, Harrick Plasma) under 300 mTorr vacuum for 15 minutes. During this time, a dilute (0.05% v/v) solution of CDTPA surface initiator (20 μL) in dry

toluene (40 mL) was prepared. Promptly after removing the open Petri dish from the plasma cleaner, the CDTPA solution was poured into the dish and covered. It then was protected from natural light with aluminum foil and left to soak in solution for 40 h at room temperature. After the allotted time the wafers/glass slides were rinsed with toluene followed by ethanol and dried under a stream of nitrogen. To maintain surface initiator integrity, substrates were stored in an inert nitrogen glovebox prior to use.

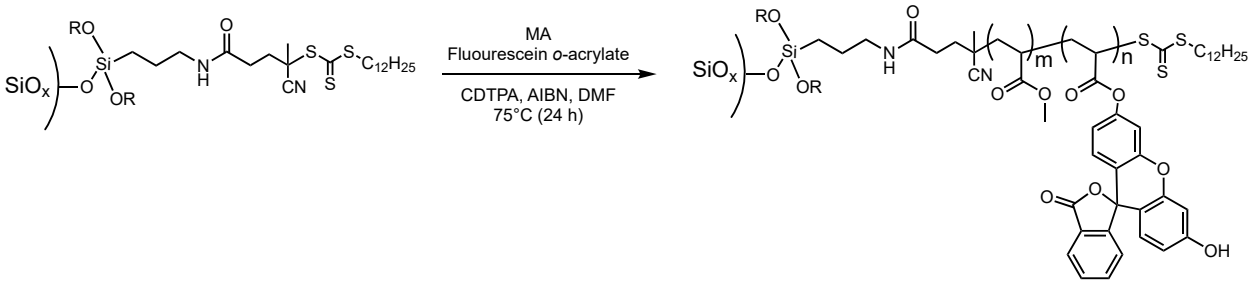
Disclaimer: For swelling measurements, silicon wafers were broken into ~ 1 cm × 2.5 cm for the liquid cell.

General procedure for the functionalization of glass beads

A 3:1 v/v sulfuric acid to hydrogen peroxide piranha solution was used to clean and activate the glass beads. Note: piranha solutions can be very dangerous. Always be careful when working with piranha solution as it is highly corrosive and may form potentially explosive peroxides. Sulfuric acid was heated to 60°C, and then hydrogen peroxide was slowly added. The solution heated to 100°C while stirring slowly, and then the beads were added. The glass beads were exposed to the piranha solution for at least 30 minutes before the solution was gently poured over ice. Deionized water (DIW) was added to the beaker with beads and left to soak for 10 minutes. Glass beads were rinsed with DIW three more times before being transferred to a round bottom flask. The beads were then dried in vacuum for 30 minutes, followed by a drying oven at 100°C for 20 minutes. Once dried, the beads were immersed in a filtered anhydrous solution of 0.05% v/v of the CDTPA initiator in toluene for 16 hours. After curing at 110°C for 1 hour, the beads were washed thoroughly with toluene and ethanol and dried in vacuo. To maintain surface initiator integrity, substrates were stored in an inert nitrogen glovebox prior to use.

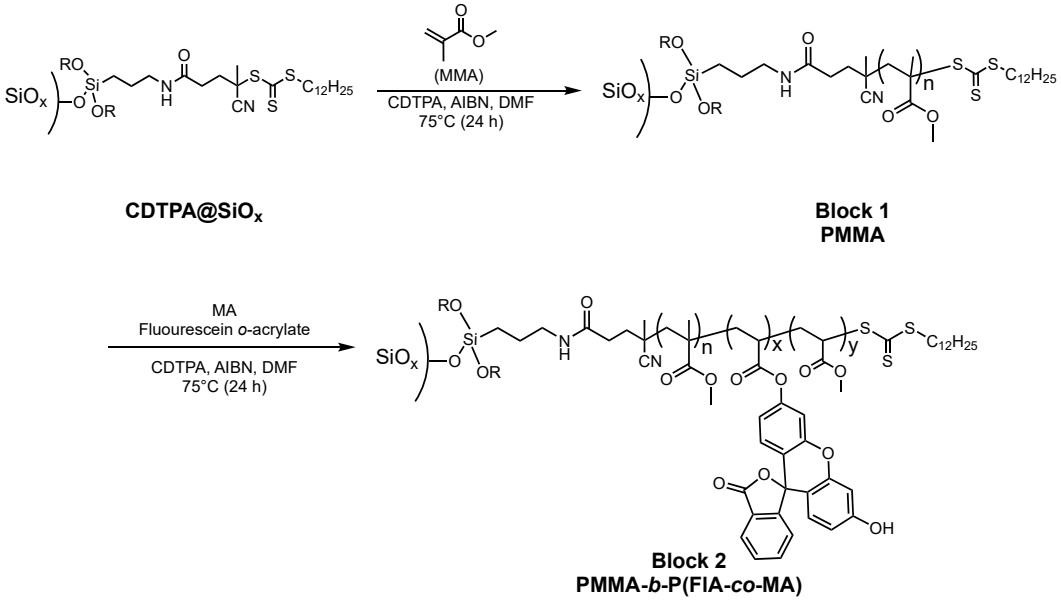
Synthesis of Polymer Brush Functionalized Substrates

Random Copolymerization of unprotected poly(fluorescein o-acrylate-co-methyl acrylate)



Methyl acrylate (MA) was purified through a basic alumina column to remove inhibitor prior to use. For copolymerization, a stock solution was prepared of inhibitor-free monomer (MA), fluorescein *o*-acrylate (FlA), sacrificial CTA 4-Cyano-4-[dodecylsulfanylthiocarbonyl)sufanyl] pentanoic acid (CDTPA), and 2,2'-azobis(2-methylpropionitrile) (AIBN). A molar ratio of [MA]:[FlA]:[CDTPA]:[AIBN] = 500:50:1:0.25 was targeted to achieve 10% fluorescein to MA polymer brushes. The stock solution was sparged under nitrogen for 15 minutes before being transferred into the glovebox. In the glovebox, anhydrous dimethylformamide (DMF) was added to the stock solution as a solvent before the solution was distributed into individual 20 mL vials that carried the functionalized CDTPA substrates. Once the substrates were fully covered with reaction solution, the reaction vials were then capped and heated to 75°C. After 24 hours, the polymer functionalized SiO_x substrates were washed with DCM and methanol. Beads were and dried in vacuo.

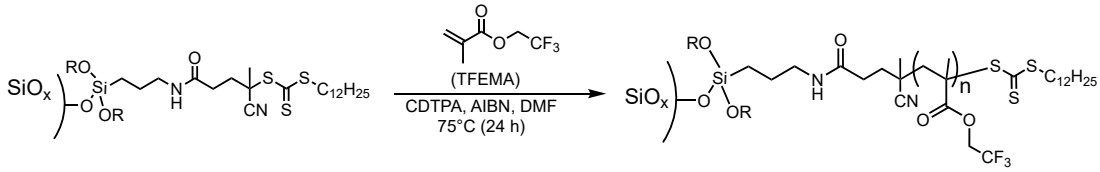
Protected diblock copolymer of PMMA-b-P(FlA-co-MA) substrates



Block 1: Methyl methacrylate (MMA) was purified through a basic alumina column to remove inhibitor prior to use. A molar ratio of [MMA]:[CDTPA]:[AIBN] = 100:1:0.25 was targeted to create a short hydrophobic underlayer close to the surface. The stock solution of the MMA, CDTPA, and AIBN was sparged under nitrogen for 15 minutes before being transferred into the glovebox. In the glovebox, anhydrous dimethylformamide (DMF) was added to the stock solution as a solvent before the solution was distributed into individual 20 mL vials that carried the functionalized CDTPA substrates. Once the substrates were fully covered with reaction solution, the reaction vials were then capped and heated to 75°C. After 6 hours, the polymer functionalized SiO_x substrates were washed with DCM and dried (beads in vacuo and silicon wafers under a stream of nitrogen).

Block 2: The PMMA substrates were chain extended with a copolymerized molar ratio of [MA]:[FlA]:[CDTPA]:[AIBN] = 500:50:1:0.25 to achieve a 10% fluorescein to MA polymer brushes outer layer. The stock solution was sparged under nitrogen for 15 minutes before being transferred into the glovebox. In the glovebox, anhydrous dimethylformamide (DMF) was added to the stock solution as a solvent before the solution was distributed into individual 20 mL vials that carried the functionalized PMMA substrates. Once the substrates were fully covered with reaction solution, the reaction vials were then capped and heated to 75°C. After 24 hours, the polymer functionalized SiO_x substrates were washed with DCM and methanol. Beads were dried in vacuo. Wafers were dried under a stream of nitrogen.

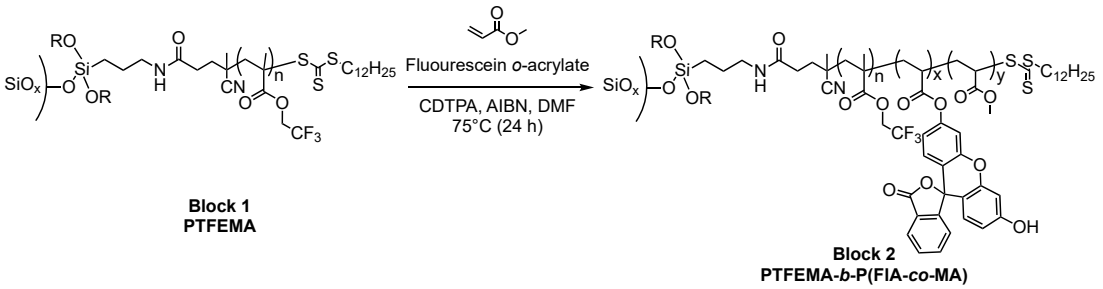
Protected diblock copolymer of PTFEMA-b-P(FlA-co-Monomer) substrates



CDTPA@SiO_x

Block 1
PTFEMA

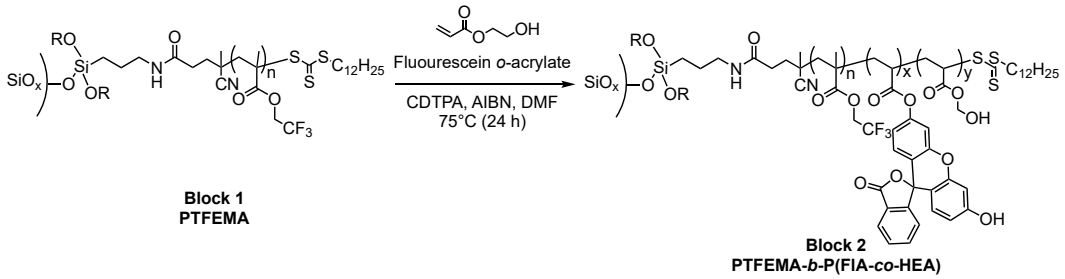
<u>Block 1</u>: 2,2,2-trifluoroethyl methacrylate (TFEMA) was purified through a basic alumina column to remove inhibitor prior to use. A molar ratio of [TFEMA]:[CDTPA]:[AIBN] = 100:1:0.25 was targeted to create a short hydrophobic underlayer close to the surface. The stock solution of the TFEMA, CDTPA, and AIBN was sparged under nitrogen for 15 minutes before being transferred into the glovebox. In the glovebox, anhydrous dimethylformamide (DMF) was added to the stock solution as a solvent before the solution was distributed into individual 20 mL vials that carried the functionalized CDTPA substrates. Once the substrates were fully covered with reaction solution, the reaction vials were then capped and heated to 75°C. After 6 hours, the polymer functionalized SiO_x substrates were washed with DCM and dried. Beads were dried in vacuo, where silicon wafers and glass slides were dried under a stream of nitrogen.



Block 1
PTFEMA

Block 2
PTFEMA-*b*-P(FlA-*co*-MA)

<u>Block 2</u> – **MA:** The PTFEMA substrates were chain extended with a copolymerized molar ratio of [MA]:[FlA]:[CDTPA]:[AIBN] = 500:50:1:0.25 to achieve a 10% fluorescein to MA polymer brushes outer layer. The stock solution was sparged under nitrogen for 15 minutes before being transferred into the glovebox. In the glovebox, anhydrous dimethylformamide (DMF) was added to the stock solution as a solvent before the solution was distributed into individual 20 mL vials that carried the functionalized PTFEMA substrates. Once the substrates were fully covered with reaction solution, the reaction vials were then capped and heated to 75°C. After 24 hours, the polymer functionalized SiO_x substrates were washed with DCM and methanol. Beads were dried in vacuo. Wafers and glass slides were dried under a stream of nitrogen.



Block 1
PTFEMA

Block 2
PTFEMA-*b*-P(FlA-*co*-HEA)

Block 2 – **HEA:** The PTFEMA substrates were chain extended with a copolymerized molar ratio of [HEA]:[FlA]:[CDTPA]:[AIBN] = 500:50:1:0.25 to achieve a 10% fluorescein to HEA polymer brushes outer layer. The stock solution was sparged under nitrogen for 15 minutes before being transferred into the glovebox. In the glovebox, anhydrous dimethylformamide (DMF) was added to the stock solution as a solvent before the solution was distributed into individual 20 mL vials that carried the functionalized PTFEMA substrates. Once the substrates were fully covered with reaction solution, the reaction vials were then capped and heated to 75°C. After 24 hours, the polymer functionalized SiO_x substrates were washed with DCM and methanol. Beads were dried in vacuo. Wafers and glass slides were dried under a stream of nitrogen.

Chain end removal (CER) of polymer brush substrates

The procedure was adapted from Chen et al. *J. Polym. Sci. Part A Polym. Chem.* 2009, *47* (23), 6704–6714.[1] A 20 mL vial was charged with AIBN (20 equiv.), LPO (2 equiv.), and the polymer brush functionalized substrates. The vial was transferred into glovebox for the addition of anhydrous toluene. The reaction stirred at 80°C for 4 hours under inert conditions, and then was quenched on ice. The substrates were washed with DCM and methanol before dried. Beads were dried under vacuo, wafers and glass slides were dried under a stream of nitrogen.

Disclaimer: The functionalization of sand followed the same procedures as above. Sand was used in place of glass beads during the piranha and grafting of CDTPA process.

Surface Characterization of Polymer Brush Functionalized Substrates

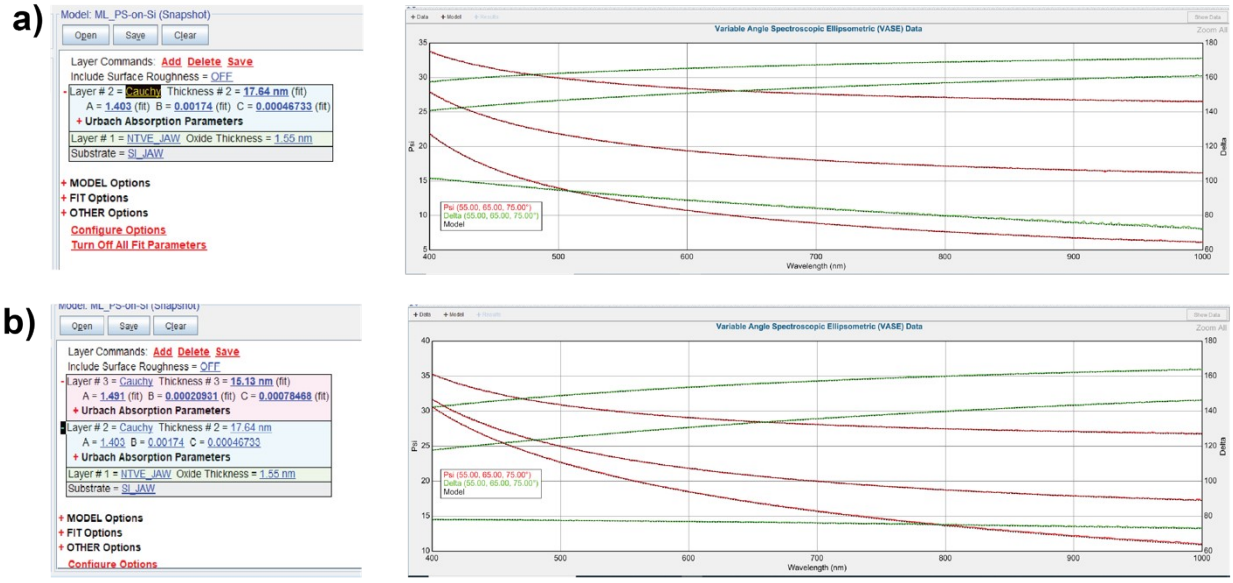


Figure S2. Example of an ellipsometry fitting model for normal, dry wafers on VASE for (a) hydrophobic block 1 (e.g., PTFEMA) and (b) chain extended photoactive polymer brush block 2 [e.g., PTFEMA-*b*-P(FlA-*co*-MA].

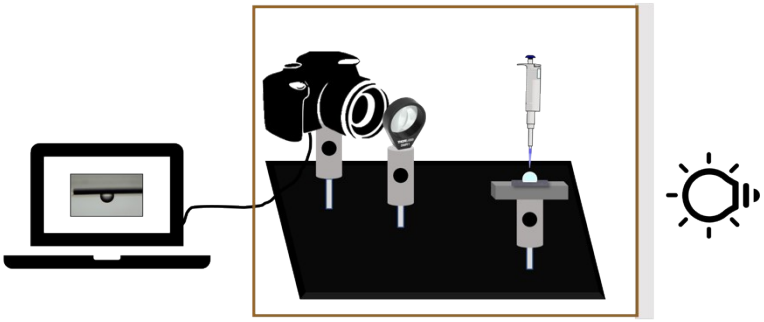


Figure S3. Schematic of setup for house set-up for in lab water contact angle measurements, employing a USB webcam (Hotpet 5 MPixel webcam) connected to a laptop, plano-convex lens with focal length *f* = 50 mm, and sample platform. A micropipette was used to deposit a drop of 5 μL of DIW onto the sample surface for imaging. The webcam was then adjusted as needed to focus and optimize sharpness. Then the setup was covered with a cardboard box with the front panel replaced with a white sheet of polypropylene. A fluorescent utility lamp was used as a backlight outside of the box, passing through the sheet of polypropylene for a uniform, lighted background. Images were captured using the webcam on the laptop. The substrates were dried with a stream of air between each measurement. The WCA was measured three times on one substrate on different areas of the wafer. WCAs were fit using the "Both Bestfits" option within the contact angle plugin for ImageJ developed by Macro Brugnara (https://imagej-nih-gov.ezaccess.libraries.psu.edu/ij/plugins/contact-angle.html).

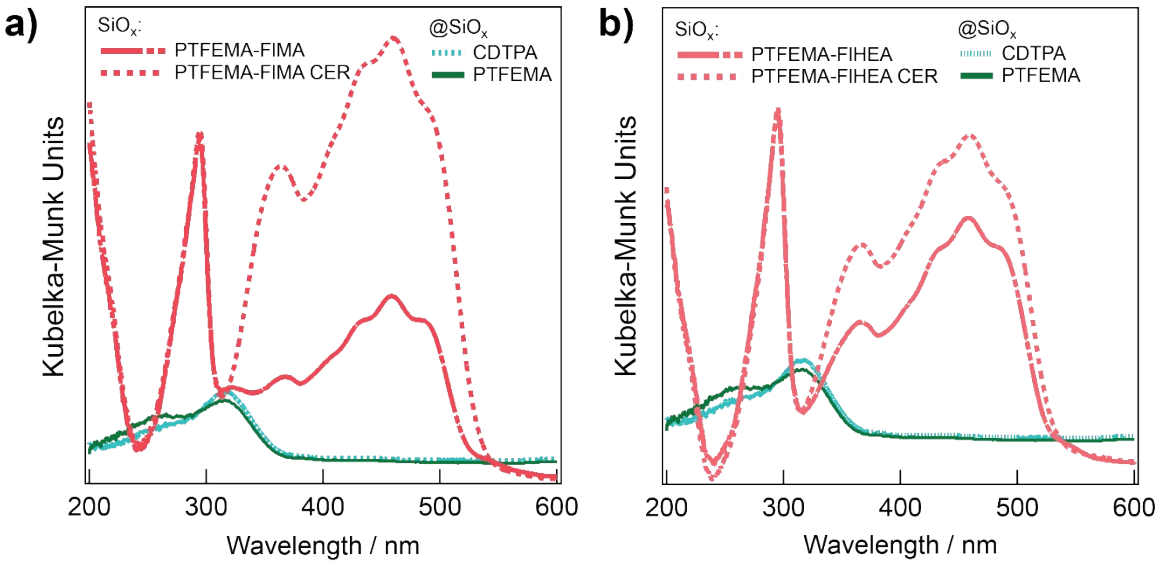


Figure S4. UV/vis DR spectra for both (a) PTFEMA-FIMA@SiO_x and (b) PTFEMA-FIHEA@SiO_x substrates compared to when its chain end is removed.

Stability Studies

A 20 mL vial equipped with a stir bar was packed with ~2000 mg of the desired polymer brush bead substrates, followed by the addition of 4 mL deionized water (DIW). The vials were stirred in the dark (covered with alumina foil) for a week. Aliquots for ^{1}H NMR (50 μL in 500 mL DMSO-d_6) and UV/vis (100 μL in 3 mL DIW) were performed daily. Aliquots were meticulously measured to ensure each sample had approximately the same amount to quantitatively compare each sample.

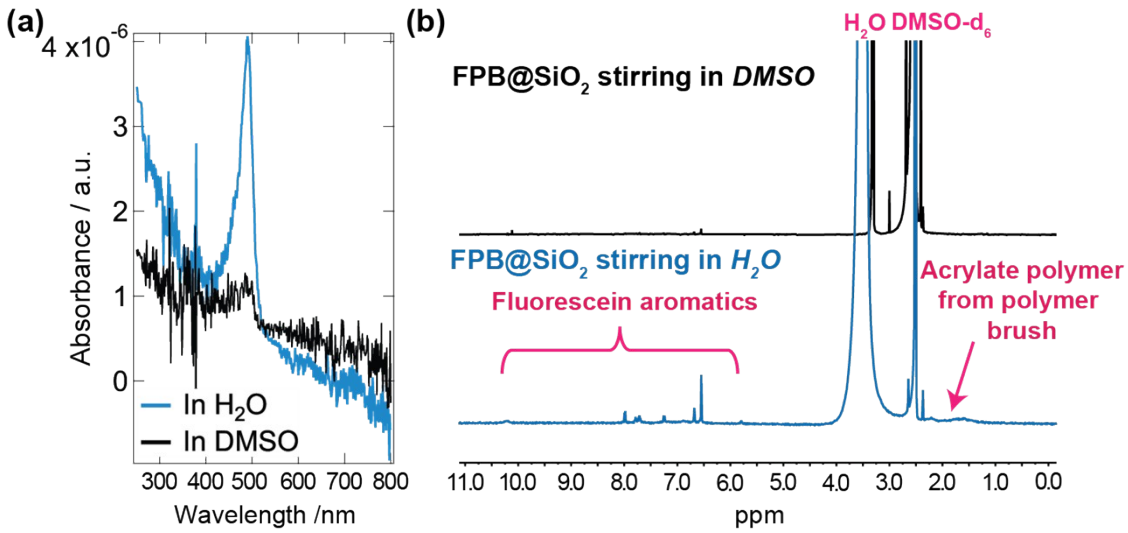


Figure S5. Apparent leaching in water but not DMSO as seen in (a) UV/vis characteristic fluorescein peak and (b) ^{1}H NMR depicting both fluorescein and acrylate polymer peaks.

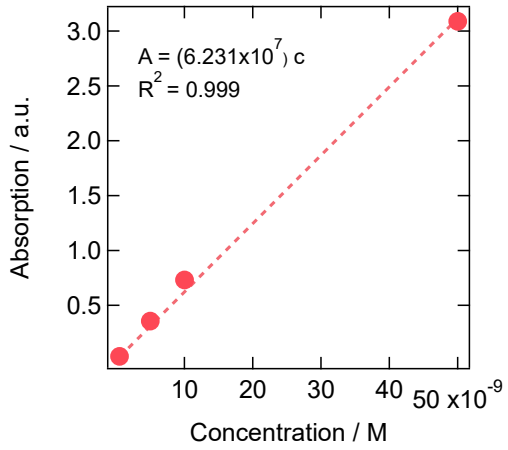


Figure S6. Calibration curve of fluorescein sodium salt to determine the concentration of fluorescein polymer brushes hydrolyzing.

Reactor Set-up

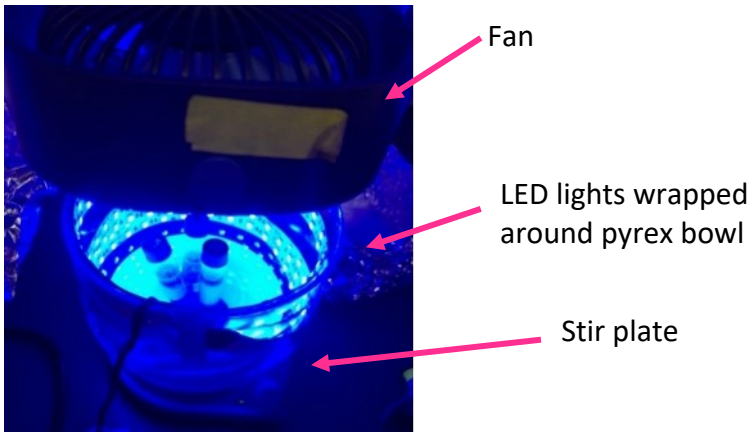
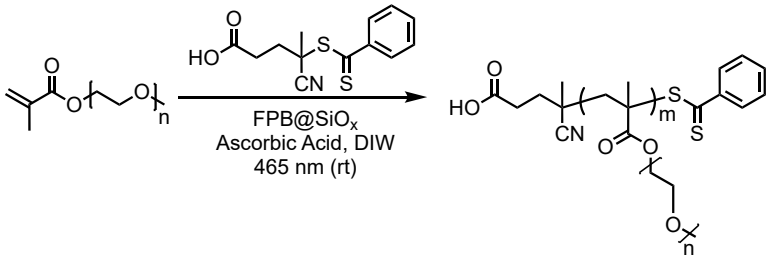


Figure S7. Experimental LED photoreactor set up for PET-RAFT polymerizations.

LED light strips ("Double Row 4 in1 RGBW 5050 LED Strip, 24V") were purchased from LEDlightinghut.com and used as shown in **Figure S9**. The RGB LED strips were connected to a rotary knob (RGB LED controller) from LEDlightinghut.com to change intensities and color of the light. The blue LED lights are λ_{max} = 465 nm (8000 lux). Lux light intensity was determined with the "Trendbox Digital Light Meter Tester Luxmeter Luminometer Photometer High Accurate 200000 Lux/FC HS1010A with LCD Display Handheld Portable" purchased through Amazon.com at the center of the light bath. Reactions were taped down in the center of the light reactor under vigorous stirring, while cooled with a fan at the highest setting. A SmartDevil small personal USB desk fan was purchased from Amazon.com and used to maintain constant temperature.

General procedure for PET-RAFT polymerization of poly(ethylene glycol)methyl ether methacrylate (PEGMEMA) monomer with protected heterogeneous photocatalysts



A 4 mL vial equipped with a magnetic stir bar and cap was charged with ~1000 mg of the desired fluorescein photocatalytic polymer brush glass beads, CPADB (1 equiv., 0.0175 mmol, 4.9 mg), PEGMEMA (300 g mol^{-1}, 200 equiv., 3.5 mmol, 1 mL), ascorbic acid (2 equiv., 0.035 mmol, 6.2 mg), and 1 mL deionized water (DIW). The reaction was vigorously stirred under blue, 465 nm LEDs with a fan being used to maintain ambient temperature. Aliquots were taken periodically to monitor the conversion and growth of the polymer of the polymerizations through ^{1}H NMR. Once the desired time had passed, the vials were wrapped in aluminum foil and placed in the freezer for five minutes. The beads were subsequently washed and filtered with methanol and dried under vacuo.

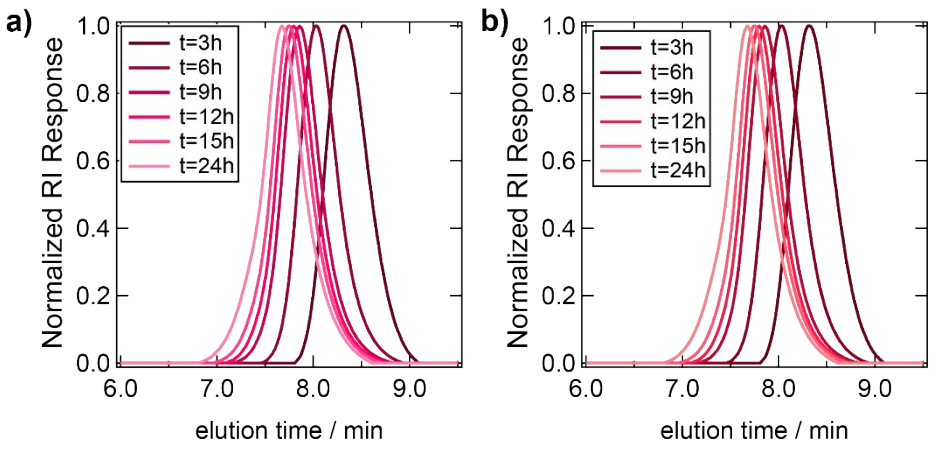


Figure S8. GPC elution curves for the kinetic study of aqueous PET-RAFT of PEGMEMA catalyzed by (a) (SiO_x)-[F|FlA-MA] and (b) (SiO_x)-[F|FlA-HEA].

General procedure for control experiments for PET-RAFT polymerization of PEGMEMA

No PC – A 4 mL vial equipped with a magnetic stir bar and cap was charged with CPADB (1 equiv., 0.0175 mmol, 4.9 mg), PEGMEMA (300 g mol^{-1}, 200 equiv., 3.5 mmol, 1 mL), ascorbic acid (2 equiv., 0.035 mmol, 6.2 mg), and 1 mL deionized water (DIW). The reaction was vigorously stirred under blue, 465 nm LEDs with a fan being used to maintain ambient temperature for 12 hours. An aliquot was taken to monitor conversion and M_n via ^1H NMR (D_2O) and dispersity via GPC (THF).

Dark – A 4 mL vial equipped with a magnetic stir bar and cap was charged with ~1000mg of PTFEMA-FlMA@SiO_x or PTFEMA-FlHEA@SiO_x beads, CPADB (1 equiv., 0.0175 mmol, 4.9 mg), PEGMEMA (300 g mol^{-1}, 200 equiv., 3.5 mmol, 1 mL), ascorbic acid (2 equiv., 0.035 mmol, 6.2 mg), and 1 mL deionized water (DIW). The reaction was wrapped in aluminum foil to prevent light exposure and vigorously stirred under a fan being used to maintain ambient temperature for 12 hours. An aliquot was taken to monitor conversion and M_n via ^1H NMR (D_2O) and dispersity via GPC (THF).

No CPADB – A 4 mL vial equipped with a magnetic stir bar and cap was charged with ~1000mg of PTFEMA-FlMA@SiO_x or PTFEMA-FlHEA@SiO_x beads, PEGMEMA (300 g mol^{-1}, 200 equiv., 3.5 mmol, 1 mL), ascorbic acid (2 equiv., 0.035 mmol, 6.2 mg), and 1 mL deionized water (DIW). The reaction was vigorously stirred under blue, 465 nm LEDs with a fan being used to maintain ambient temperature for 12 hours. An aliquot was taken to monitor conversion and M_n via ^1H NMR (D_2O) and dispersity via GPC (THF).

No Ascorbic Acid – A 4 mL vial equipped with a magnetic stir bar and cap was charged with ~1000mg of PTFEMA-FlMA@SiO_x or PTFEMA-FlHEA@SiO_x beads, CPADB (1 equiv., 0.0175 mmol, 4.9 mg), PEGMEMA (300 g mol^{-1}, 200 equiv., 3.5 mmol, 1 mL), and 1 mL deionized water (DIW). The reaction was vigorously stirred under blue, 465 nm LEDs with a fan being used to maintain ambient temperature for 12 hours. An aliquot was taken to monitor conversion and M_n via ^1H NMR (D_2O) and dispersity via GPC (THF).

Homogeneous, small molecule – A 4 mL vial equipped with a magnetic stir bar and cap was charged with CPADB (1 equiv., 0.0175 mmol, 4.9 mg), PEGMEMA (300 g mol^{-1}, 200 equiv., 3.5 mmol, 1 mL), and ascorbic acid (2 equiv., 0.035 mmol, 6.2 mg). A stock solution of fluorescein (free acid) was created in deionized water (DIW) to create a concentration of 1 mg mL^{-1}. The photocatalyst from the stock solution was added to the vial (0.025 equiv., 0.0004, 0.165 mL), followed by DIW (0.835 mL). The reaction was vigorously stirred under blue, 465 nm LEDs with a fan being used to maintain ambient temperature for 12 hours. An aliquot was taken to monitor conversion and M_n via ^1H NMR (D_2O) and dispersity via GPC (THF).

Table S1: Summary of the PET-RAFT polymerization of PEGMEMA results in comparison to control experiments after 12 hours.

Experimental Conditions	Conversion[a]	$M_{n,Theo}$ (g mol^{-1})	$M_{n,NMR}$ (g mol^{-1})[b]	$Đ$[c]
PTFEMA-FlMA@SiO$_x$[d]	28%	16,500	20,400	1.12
PTFEMA-FlHEA@SiO$_x$[d]	73%	43,600	41,200	1.29
No PC[e]	-	-	-	-
No Irradiation[f]	-	-	-	-
Bare, unfunctionalized[g] beads	-	-	-	-
No CPADB[h]	41%	24,800	272,500[k]	3.22
No Ascorbic Acid[i]	58%	35,000	30,300	1.31
Fluorescein, sodium salt[j]	55%	33,100	27,800	1.27

All polymerizations were performed in DIW at RT under blue λ_{max} = 465 nm LED irradiation for 12 hours unless otherwise noted. [a]Monomer conversion determined by ^{1}H NMR. [b]Molecular weight determined via chain end analysis in ^{1}H NMR. [c]Molecular weight distribution determined via GPC in THF using universal calibrations. [d]~1000 mg beads added. [e]No photocatalyst was added. [f]Reaction performed in the dark for both PTFEMA-FlMA@SiO$_x$ and -FlHEA@SiO$_x$ beads. [g]No photocatalyst, but ~1000mg of bare, unfunctionalized glass beads added. [h]~1000mg FTFEMA-FlHEA@SiO$_x$ added, no CPADB added. [i]~1000mg FTFEMA-FlHEA@SiO$_x$ added, no ascorbic acid added. [j]Fluorescein, free acid (0.025 equiv., 0.0004 mmol) added as a control homogeneous reaction. [k]Molecular weight determined via GPC in THF using universal calibrations due to no evidence of chain ends in ^{1}H NMR.

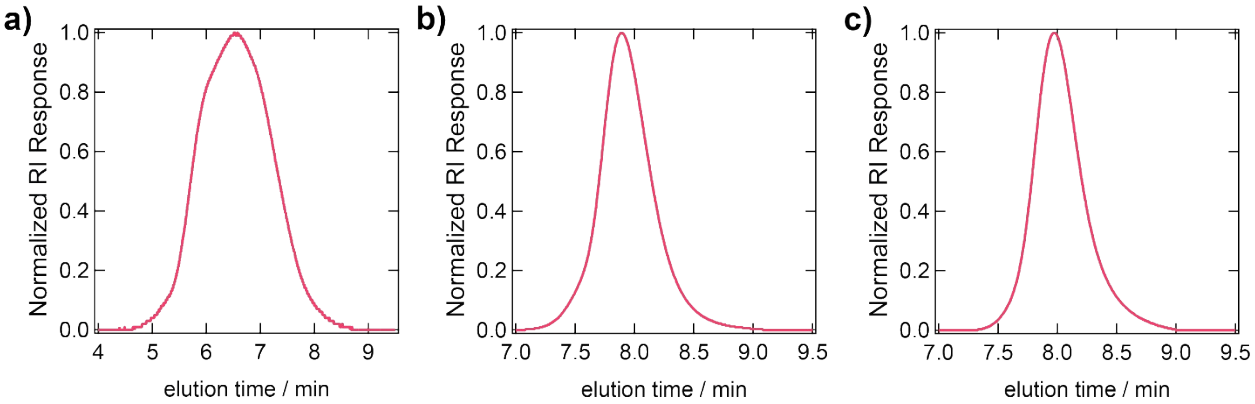


Figure S9. GPC elution curves for control experiments of (a) no CPADB added, (b) no ascorbic acid, and (c) fluorescein homogeneous in the aqueous PET-RAFT of PEGMEMA.

Swelling Studies

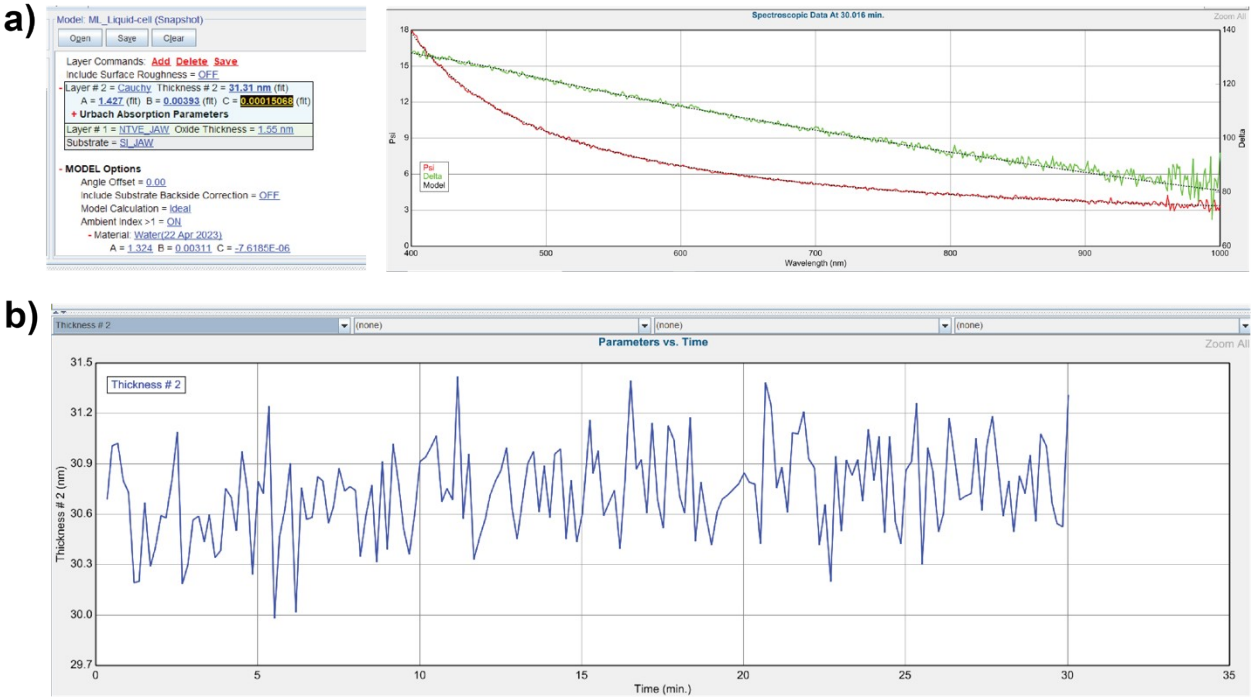


Figure S10. Example of an ellipsometry fitting model for wafers in the liquid sample cell injected with DIW on VASE for (a) the swelling of PTFEMA-*b*-P(FlA-*co*-HEA) and its (b) average thickness over a 30 minute equilibrium time period.

Environment Studies

General procedure for acidic conditions for PET-RAFT polymerization of PEGMEMA

A pH ~ 4 stock solution was created by adding hydrochloric acid (HCl) dropwise into 10 mL DIW until desired pH was achieved. The pH was monitored by pH paper. A was 4 mL vial equipped with a magnetic stir bar and cap was charged with ~1000 mg of PTFEMA-*b*-P(FlA-*co*-HEA) CER glass beads, CPADB (1 equiv., 0.0175 mmol, 4.9 mg), PEGMEMA (300 g mol^{-1}, 200 equiv., 3.5 mmol, 1 mL), ascorbic acid (2 equiv., 0.035 mmol, 6.2 mg), and 1 mL acidic DIW. The reaction was vigorously stirred under blue, 465 nm LEDs with a fan being used to maintain ambient temperature. Aliquots were taken periodically to monitor the conversion and growth of the polymer of the polymerizations through ^{1}H NMR. Once the desired time had passed, the vials were wrapped in aluminum foil and placed in the freezer for five minutes. The beads were subsequently washed and filtered with methanol and dried under vacuo.

General procedure for basic conditions for PET-RAFT polymerization of PEGMEMA

A pH ~ 10 stock solution was created by adding sodium hydroxide (NaOH) dropwise into 10 mL DIW until desired pH was achieved. The pH was monitored by pH paper. A was 4 mL vial equipped with a magnetic stir bar and cap was charged with ~1000 mg of PTFEMA-*b*-P(FlA-*co*-HEA) CER glass beads, CPADB (1 equiv., 0.0175 mmol, 4.9 mg), PEGMEMA (300 g mol^{-1}, 200 equiv., 3.5 mmol, 1 mL), ascorbic acid (2 equiv., 0.035 mmol, 6.2 mg), and 1 mL basic DIW. The reaction was vigorously stirred under blue, 465 nm LEDs with a fan being used to maintain ambient temperature. Aliquots were taken periodically to monitor the conversion and growth of the polymer of the polymerizations through ^{1}H NMR. Once the desired time had

passed, the vials were wrapped in aluminum foil and placed in the freezer for five minutes. The beads were subsequently washed and filtered with methanol and dried under vacuo.

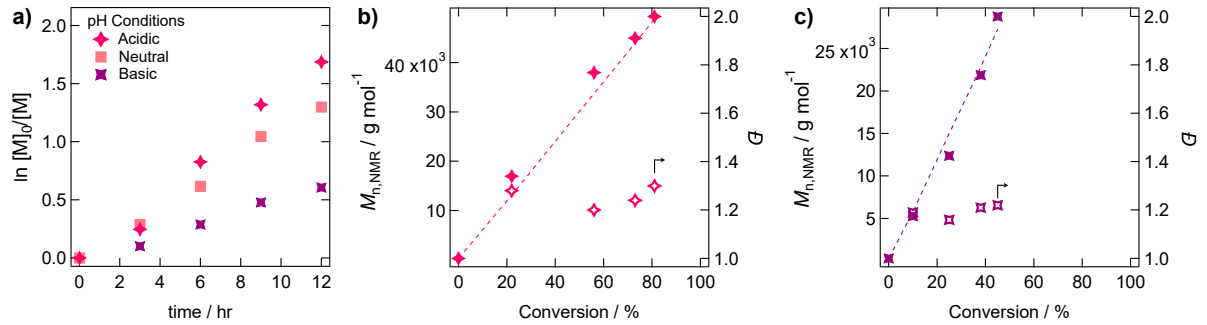


Figure S11. (a) The kinetic plot of aqueous PET-RAFT of PEGMEMA under various pH conditions using (SiO_x)-[F|FlA-HEA]. The number-average molecular weight (as determined by ^{1}H-NMR) and dispersity (obtained via GPC) as a function of PEGMEMA monomer conversion for PET-RAFT under (b) acidic conditions (pH ~ 4) and (c) basic conditions (pH ~ 10). The dashed/dotted lines indicate the theoretical molecular weight for each conversion.

General procedure for bead amount studies for PET-RAFT polymerization of PEGMEMA

A 4 mL vial equipped with a magnetic stir bar and cap was charged with either ~500 mg or ~2000mg of PTFEMA-*b*-P(FlA-*co*-HEA) CER glass beads glass beads depending on the desired study, CPADB (1 equiv., 0.0175 mmol, 4.9 mg), PEGMEMA (300 g mol^{-1}, 200 equiv., 3.5 mmol, 1 mL), ascorbic acid (2 equiv., 0.035 mmol, 6.2 mg), and 1 mL deionized water (DIW). The reaction was vigorously stirred under blue, 465 nm LEDs with a fan being used to maintain ambient temperature. Aliquots were taken periodically to monitor the conversion and growth of the polymer of the polymerizations through ^{1}H NMR. Once the desired time had passed, the vials were wrapped in aluminum foil and placed in the freezer for five minutes. The beads were subsequently washed and filtered with methanol and dried under vacuo.

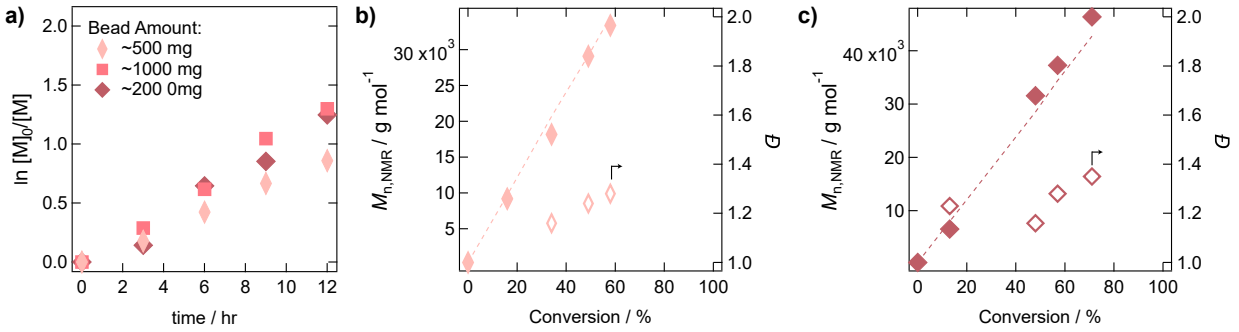


Figure S12. (a) The kinetic plot of aqueous PET-RAFT of PEGMEMA varying (SiO_x)-[F|FlA-HEA] glass bead loading. The number-average molecular weight (as determined by ^{1}H-NMR) and dispersity (obtained via GPC) as a function of PEGMEMA monomer conversion for PET-RAFT with (b) ~500 mg (50% of the normal conditions) and (c) ~2000 mg (2x the normal conditions). The dashed/dotted lines indicate the theoretical molecular weight for each conversion.

General procedure for varying the monomer scope for PET-RAFT polymerization of PEGMEMA

A 4 mL vial equipped with a magnetic stir bar and cap was charged with ~1000 mg of PTFEMA-*b*-P(FlA-*co*-HEA) CER glass beads glass beads, CTA (1 equiv., 0.0175 mmol), monomer (200 equiv., 3.5 mmol), ascorbic acid (2 equiv., 0.035 mmol, 6.2 mg), and 1 mL deionized water (DIW). See table below for matching CTA and monomer set. The reaction was vigorously stirred under blue, 465 nm LEDs with a fan being used to maintain ambient temperature. Aliquots were taken periodically to monitor the conversion and growth of the polymer of the polymerizations through ^{1}H NMR. Once the desired time had passed, the vials were wrapped in aluminum foil and placed in the freezer for five minutes. The beads were subsequently washed and filtered with methanol and dried under vacuo.