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The Design and Synthesis of Y-shaped ROP/RAFT Binary Initiators to Impart Multiple Functionalities in Surface Coatings

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A thesis submitted in partial fulfillment of the requirements for a baccalaureate degree in Chemistry with honors in Chemistry

Reviewed and approved* by the following:

Christian W. Pester Professor of Chemical Engineering Thesis Supervisor

> Elizabeth Elacqua Professor of Chemistry Honors Adviser

> Julie Fenton Professor of Chemistry Faculty Reader

* Electronic approvals are on file.

ABSTRACT

Generating polymer brushes from surface-initiated polymerizations (SI-P), or "grafting from" an initiator bound to a surface is a powerful technique which allows for facile design and functionalization of durable surface coatings. This project takes advantage of a ring-opening reaction of an epoxide to impart multiple functionalities into polymer surface coatings with two distinct polymerization methods initiated from a single "Y-shaped" molecule. Ring-opening polymerization (ROP) and reversible addition-fragmentation chain-transfer (RAFT) polymerization are two separate living polymerizations that can be used to assemble polymer brushes. A Y-shaped binary initiator gives the ability for both ROP and RAFT polymerizations to be combined on one molecule, and thus more uniformly distributed along a surface. This method makes it possible to implement multiple functionalities into surface coatings from a singular surface tethered initiator.

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Chapter 1

Background

1.1 The History and Principles of Polymer Brushes

Modern chemical research has inspired new applications within the fields of polymer science and surface engineering. Polymer brushes are layers of thin polymer films that are covalently attached to the surface. In the 1950s researchers discovered a new way to prevent flocculation by grafting polymer molecules to colloidal particles.¹ Since this discovery, researchers have described various polymerization methods which have galvanized industrial and scientific advances. Creating polymer brushes with surface-initiated controlled polymerization, or "grafting from" has allowed for powerful manipulation of both the chemical and physical properties of surfaces. Furthermore, the chemical diversification of surfaces provides the potential to supply additional features which can enhance product design and functionality. Polymer surface coatings provide a wide range of applications from corrosion resistance to superhydrophilic coatings which can prevent fogging or frosting.²

Surface tethered polymer brushes can be divided into homopolymer brushes, random copolymer brushes, block copolymer brushes, and mixed homopolymer brushes.¹ Homopolymer brushes consist of repeat units of a single monomer species to produce a polymer chain tethered to the surface (Figure 1a). Random copolymer brushes are named for the random distribution of multiple different monomer species within the polymer chains. Block copolymer brushes are two or more homopolymer chains covalently connected to each other in a "stacked" formation and attached to the surface. Finally, *mixed* homopolymer brushes are vaguely described in the

literature as "two or more homopolymer chains tethered to a surface".^{3,4} Conventional mixed homopolymer brushes on the surface involve two or more randomly dispersed homopolymer chains that can selectively respond to various stimuli (see Figure 1b). Their numerous potential applications in catalysis, drug delivery, and functional surface coatings have motivated scientists to further investigate mixed polymer dynamics.^{4,5,6} Overall, mixed homopolymer brushes maximize the potential for diversification of surfaces, allowing for multiple differentiable polymer chains to adhere to a singular surface. Mixed homopolymer brushes are not broadly used due to their limitations including unequal distribution of the brushes on the surface and an inability to precisely characterize mixed homopolymer surfaces.⁶ Conventional mixed homopolymer brushes use two radical techniques, which may result in unwanted side reactions between initiators. Proposing a radical technique alongside a cationic technique will reduce the possibility of side reactions, and therefore enhance the feasibility of two homopolymer brushes side by side in a uniform conformation across the surface. This project will outline the creation of a single Y-shaped surface initiator that assures even distribution of mixed homopolymer brushes (see Figure 1c). Further, the initiator will allow for selective ROP/RAFT polymerizations from their respective side chains with minimal interference.



Figure 1 Illustration of polymer brushes on the surface: (**a**) homopolymer brush (**b**) conventional mixed homopolymer brush (**c**) mixed homopolymer brush of proposed Y-shaped binary initiator. The proposed Y-shaped binary initiator will ensure uniform distribution of mixed homopolymer brushes.

1.2 Polymerization

A polymerization event refers to a chemical process in which small subunits, or monomers, covalently bond to produce a larger chain-like macromolecule. Polymerization reactions are classified into two broad categories – addition polymerization and condensation polymerization. Addition polymerization, or chain-growth polymerization, is used in countless industrial processes globally to produce polymers of high molecular weight.⁴

Chain-growth polymerization occurs when monomer units are added one at a time to a growing polymer chain via sequential addition. All chain-growth polymerization reactions require two initial steps: chain initiation and chain propagation. Many chain-growth polymerizations also feature chain transfer and termination, yet these steps can be largely avoided to improve control over the reaction (e.g., ionic polymerization). Chain initiation occurs when energy is provided to generate a reactive intermediate such as a charged molecule or unpaired electron (radical). The required energy can be provided in several forms: thermal, chemical, etc. Once the polymerization has begun, propagation refers to the continued addition of monomers to the active chain end. A termination of chain propagation occurs when the reactive intermediates interact. For example, in radical polymerization, polymer chains can terminate via disproportionation or recombination.

Three examples for chain-growth polymerizations are anionic, cationic, and radical polymerization. The ionic polymerizations, anionic and cationic, are initiated by a nucleophile creating a carbanion and an acid creating a carbocation, respectively. These carbanions and carbocations then act as initiators.⁷ Cationic ring-opening polymerization (CROP) will be one of two methods used on the Y-shaped binary initiator in this project.

Figure 2 outlines a general schematic of the CROP polymerization used in this study. The hydrogen ions created upon photo initiation react with δ -valerolactone, the monomer, creating a carbocation. The carbocation is then attacked by the cationic polymerization initiator, a hydroxyl group. The resulting polymer chain is unique in its incorporation of lactone functional groups in the chain itself.



Figure 2 Cationic ring-opening polymerization of δ -valerolactone

Conversely, radical polymerizations propagate from a carbon radical created by a radical initiator.⁸ RAFT polymerizations are initiated by a free-radical source which then reacts with a single monomer. The polymerization reaction is then propagated, or continued to create radical chains with length *n*. Figure 3 outlines a general reversible addition-fragmentation chain-transfer (RAFT) polymerization of a monomer (M) which has undergone propagation, indicated by the repeating monomer units in the product.



Figure 3 General reversible addition-fragmentation chain-transfer (RAFT) polymerization

1.3 Photo-controlled Polymerization

The past several decades have unveiled several diverse photochemical methods to activate a multitude of chemical transformations.^{8,9,10} Using visible light to initiate polymer synthesis provides a safe and powerful alternative to other high energy methods (e.g., high temperatures or UV light). Polymerization methods regulated by visible light have gained popularity in recent years given the simplistic selectivity and ease of reversible deactivation.⁶ Photosensitive molecules can be externally added to solutions to induce controlled polymerization events. Boyer et al. have proposed numerous efforts to control both ROP and RAFT polymerizations via a novel photoacid (PAH) and transition metal photo-redox catalyst (ZnTPP), respectively.^{10,11} Figure 4 shows the photoacid designed by Boyer et al. along with the molecule's deprotonation with exposure to visible light.



Figure 4 Photoacid Activation for ring opening polymerization¹¹

The heightened control offered by the ability to 'activate' a cationic polymerization with visible light is also possible with a radical polymerization.^{12,13,14} This study employs a transition metal catalyst, ZnTPP as a free-radical source for RAFT polymerization upon irradiation with visible

light. Figure 5 shows the UV-Vis absorption spectra and structure of both photocatalysts used in this study.



Figure 5 UV-Vis Absorption Spectra of PAH and ZnTPP solutions.¹¹

Chapter 2

Materials and Methods

2.1 Design and Preparation of the Y-shaped Binary Initiator

Epoxides are cyclic ethers in a three-membered ring conformation that have proven to be an important class of organic compounds for synthetic reactions. Epoxides are inherently under a large degree of strain due to the geometry of a three-membered ring. Further, steric strain is present in the hydrogen atoms on the carbons as they are held in an almost eclipsed formation. This high degree of ring strain results in an increased reactivity toward nucleophiles, ultimately resulting in an S_N2 reaction with an undesired leaving group of the epoxide's oxygen. Because of the cyclic structure, the leaving group does not separate from the molecule, but is retained in the product as an alcohol group once protonated.

Most epoxide ring opening reactions in laboratory settings are driven by a Lewis acid catalyst. The harsh acidic conditions typically utilized for this type of reaction, however, have been shown to be unnecessary and would likely degrade the RAFT chain transfer agent (CTA).¹⁵ Work by Mohseni et al. shows mild and efficient reaction conditions to support the ring opening of an epoxide with alcohols.¹⁶ Using only nitromethane, a polar solvent, this simple method runs at room temperature and does not require an additional catalyst.



Figure 6 Epoxide ring opening reaction to form Y-shaped ROP/RAFT binary initiator

The Y-shaped initiator was synthesized using the reduced form, 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl] pentanol (CDTPA-OH), of a commonly used RAFT agent, 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl] pentanoic acid (CDTPA). Backside nucleophilic attack of the epoxide on (3-Glycidyloxypropyl) triethoxysilane by CDTPA-OH results in both primary alcohol and RAFT CTA chain ends. In similar reactions, Mohseni et al. reported the regioselectivity for the ring opening reaction of an asymmetric epoxide ring.¹⁶

The final product supports both ROP and RAFT polymerizations from the same molecule. Further, the silane will attach the dual initiator to silicon oxide surfaces.¹⁷ With the two separate polymer units grafting through two methods of living polymerization, two discrete functionalities can be simultaneously implemented in surface coatings.



Figure 7 Y-shaped ROP/RAFT binary initiator attached to a surface (ROP initiator shown in blue, RAFT initiator shown in red)

2.2 Solution Study Methodology

To verify that both RAFT and ROP polymerizations are successfully initiated by this Yshaped binary initiator, solution studies were performed using common, literature supported RAFT and ROP reaction conditions.^{11,18} Solution studies began with the purified Y-shaped binary initiator. An aliquot of Y-shaped binary initiator was added to a vial with Boyer et al. photoacid, an excess of δ -Valerolactone and stirred under blue light to undergo ROP.¹¹ An additional aliquot of Y-shaped binary initiator was added to a Schlenk tube with 2,2'-asobis(2methylpropionitrile) (AIBN) and methyl methacrylate (MMA) to undergo RAFT. The RAFT mixture was degassed before being stirred at 75° C. Both the ROP and RAFT polymer products were then reacted with the opposite polymerization technique to confirm the presence of the singular Y-shaped binary initiator and ability to perform these polymerizations in sequence.

Gel permeation chromatography (GPC) is a type of gel filtration, size exclusion chromatography that separates molecules based on their relative size in solution. The GPC elution profiles represent the molecular weight distributions and provide a clear quantitative difference between samples. As the polymer solutions pass through the organic gel columns with controlled pore sizes, the largest molecules elute first as they do not fit into the pores in the gel matrix. This study will utilize GPC to quantify polymer products in solution.

2.3 Surface Study Methodology

Silicon oxide wafers are commonly used in the initial stages of surface coating development. This is for several reasons including their refractive properties which allow for film thickness measurements via reflectometry-based techniques, a smooth surface for surface analysis via imaging techniques, and silanol groups which provide a facile way to covalently attach initiators with silane groups.¹⁹ These properties are essential to confirming and characterizing the Y-shaped binary initiator's presence on a surface.

This study will use ellipsometry to measure film thickness as well as X-ray photoelectron spectroscopy (XPS) to characterize chemical composition of the surface. To begin these studies, native oxide silicon oxide wafers were functionalized with the Y-shaped binary initiator. The term functionalization implies the silane group on the binary initiator becomes covalently attached to the silanol groups on the wafers. The wafers were functionalized by undergoing sonication and plasma treatment before being soaked in a toluene solution containing the Y-shaped binary initiator. Functionalization of the wafers was confirmed with both ellipsometry and XPS.

Ellipsometry remains one of the most crucial characterization techniques in the design and production of thin films. Ellipsometry is an optical technique that allows for non-destructive analysis of thin films via polarized light. A basic experimental ellipsometry setup includes a light source, polarizer, sample surface, analyzer, and detector. The specular optical technique begins with the linear polarization of electromagnetic radiation emitted from a light source. When the polarized light hits the sample, it reflects before hitting an analyzer, and finally the detector. The material properties of the sample are determined through the change in the polarization of light when the reflective interaction with the sample structure occurs. When a measurement is taken on an ellipsometer, a model must be employed to fit the data for the surface of interest. In this study the surfaces were modeled as isotropic one-polymer layers on top of a native silicon oxide layer and silicon substrate. The polymer optical properties were fit using a basic Cauchy model

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in CompleteEase software. Polymer layer thicknesses were averaged from three independent spot measurements on the surface.

X-ray Photoelectron Spectroscopy, or XPS is a technique used for the quantitative chemical analysis of surfaces. The sample surface is irradiated with X-rays which result in ejected electrons of different energies. The number and kinetic energy of electrons ejected is utilized to infer the chemical states of surfaces. This analytical technique is crucial in this study to confirm the presence of both ROP and RAFT polymer chains on the surface.

Chapter 3

Results and Discussion

3.1 Synthesis of Y-Shaped Binary Initiator

Upon completion of the synthetic reaction, the Y-Shaped Binary Initiator was purified via column chromatography before a nuclear magnetic resonance (NMR) spectrum was taken (see Figure 8).



Figure 8¹H NMR of synthesized Y-Shaped Binary Initiator

The obtained ¹H NMR showed the possibility of product formation via the presence of expected peaks. Residual CDTPA-OH was present on the spectrum, indicating the need for better purification techniques.

3.2 Solution Studies

Upon completion of both ROP and RAFT polymerization events in solution, GPC was used to characterize the polymers produced. The reported GPC results were consistent with those reported in the literature, with the ROP polymer product alone (being smallest in size) eluting out much later than its successive ROP/RAFT mixed homopolymer species (see Figure 9).¹¹



Figure 9 Solution polymerization GPC data for ROP of δ -VL (purple, solid line) followed by RAFT polymerization of MMA to give final mixed polymer chains (blue, dashed line)

The mixed polymer chains produced by RAFT polymerization followed by ROP using the Y-shaped binary initiator solution polymerization showed a much smaller shift in the GPC elution profile (Figure 10). This is due to the smaller impact of the addition of the ROP polymer chain on the size of the overall molecule versus the pure RAFT polymerization product.



Figure 10 Solution polymerization GPC data for RAFT of MMA (pink, solid line) followed by ROP polymerization of δ -VL to give final mixed polymer chains (blue, dashed line)

Both mixed polymer products were higher in molecular weight than their preceding singular homopolymer chains with negligible increases in polydispersity. The produced mixed homopolymer products show high molar masses (~ 141 KDa) with narrow molecular weight distributions (MW/MN= 1.27). Further, the individual polymerizations agreed with the current reported values under similar conditions – ROP with pVL fluctuated around 10 KDa and RAFT with pMMA around 180 KDa.¹¹

Because the binary initiator has a molecular weight of 668.10 g/mol, that value was first subtracted from the polymer molecular weight. The remaining value was divided by the molecular weight of one monomer unit – giving an approximate number of monomers in one

polymer chain. For the subsequent polymerization event, the first molecular weight was subtracted from the total value before the value was divided again by the weight of one monomer unit, yielding the approximate number of monomers in succession for the second polymerization. The observed and calculated data for both mixed polymerizations are shown in Tables 1 and 2 below.

	Monomer M/W	Polymer M/W	Approximate #	Polydispersity
	(g/mol)	(g/mol)	Monomers	
ROP	100.12	11,200	105	1.10
$ROP \rightarrow RAFT$	100.12	87,800	765	1.21

Table 1 GPC data for ring-opening polymerization in solution

There is an approximately 7:1 ratio on MMA:VL when starting with ring opening polymerization, which rises to around a 14:1 MMA:VL ratio when starting with RAFT polymerization. The higher ratio of MMA when starting with RAFT polymerization may be attributed to the slightly lower control apparent from the higher polydispersity (Table 2).

 Table 2 GPC data for RAFT polymerization in solution

	Monomer M/W	Polymer M/W	Approximate #	Polydispersity
	(g/mol)	(g/mol)	Monomers	
RAFT	100.12	182,000	1812	1.35
$RAFT \rightarrow ROP$	100.12	195,000	135	1.32

3.3 Surface Studies

Photoinduced RAFT and ROP polymerizations were used to confirm the presence of the Y-shaped binary initiator on the surface. Once wafers were functionalized with the Y-shaped binary initiator, aqueous RAFT polymerizations with [2-(methacryloyloxy)ethyl] trimethylammonium chloride (METAC) were carried out on the wafers before being quantified with ellipsometry.

The initial recorded results for RAFT polymerizations were lower in thickness than previously reported in the literature for SI-RAFT polymerization with CDTPA initiator and METAC monomer, indicating a lower grafting density. This can cause the polymer chains to appear less thick compared to a more densely packed brush, even if molecular weights are similar.^{2,20} Figure 11 illustrates the effect of more closely packed polymer chains due to increased initiator sites on the surface (Figure 11a) versus less concentrated initiator sights resulting in low grafting density (Figure 11b).



Figure 11 Comparison of high-density grafting (a) to low-density grafting (b) of surface tethered polymers.

The concentration of the Y-shaped binary initiator in toluene solution while functionalizing the wafers was increased to match the literature reported procedure in the functionalization of the native oxide silicon wafers which resulted in similar thickness values to those in previous studies (see Figure 12).²



Figure 12 RAFT kinetics with PMETAC on Y-shaped binary initiator wafers

Wafers functionalized with Y-shaped binary initiator also underwent photoinduced ringopening polymerizations on the surface. The reported results of ROP on the surface had lower thicknesses than RAFT, though this was expected according to the current literature on ROP kinetics.¹⁹



Figure 13 ROP kinetics with PVL on Y-shaped binary initiator wafers

Control experiments showed no RAFT polymer growth on unfunctionalized wafers. Further, no ROP or RAFT polymer growth occurred in the absence of PAH or ZnTPP.

XPS was able to further confirm the covalent attachment of the Y-shaped binary initiator to the surface. A wafer functionalized with the Y-shaped binary initiator underwent ROP before being split in half. The average surface thickness of the ROP wafer before being split was 6.19 nm. One half of the wafer was analyzed with XPS (see Figure 14a (gray) and 14c) while the other underwent RAFT polymerization before being analyzed with XPS (see Figure 14a (green) and 14b). After RAFT polymerization, the wafer containing both ROP/RAFT polymerizations yielded an average thickness of 8.48 nm.



Figure 14 Survey (**a**) and high-resolution carbon (**b**,**c**) XPS spectra of native oxide silicon wafers functionalized with Y-shaped binary initiator and subsequently polymerized by SI-ROP of δ -VL followed by SI-RAFT of METAC. Green lines represent mixed PVL and PMETAC chains (**b**) and gray lines represent pVL homopolymer chains (**c**).

XPS confirmed ROP with δ -valerolactone via the presence of C=O and C-O bonds in the high-resolution carbon spectrum. Further, the increase in the carbon-heteroatom bonding environment in the high-resolution carbon spectrum indicates the addition of C-N bonding environments present in METAC. Tables 3 and 4 organize the expected, or theoretical percentage of each element on the surface with the recorded, or actual percentage of each element on the surface obtained from XPS analysis.

Table 3 XPS elemental composition quantification for ROP with δ -valerolactone

Element	Theory (%)	Actual (%)
Carbon	59.98	63.42
Nitrogen	n/a	n/a
Oxygen	31.96	25.26
Silicon	n/a	11.32

The actual percentage of carbon and oxygen on the ROP with δ -valerolactone wafer was consistent with the theoretical values expected with the polymer structure. More so, the expected ratio of C-C: C-O: C=O for pVL was 4:2:1 given the monomer structure. The XPS data confirmed the presence of pVL on the surface giving an actual ratio of around 3.28:1.43:1.

Table 4 XPS elemental composition quantification for dual ROP/RAFT binary polymerization with δ -valerolactone and METAC

Element	Theory (%)	Actual (%)
Carbon	56.012	65.91
Nitrogen	3.37	1.1
Oxygen	23.69	23.54
Chlorine	8.54	1.56
Silicon	n/a	7.89

The actual percentage of carbon, nitrogen, and oxygen on the ROP/RAFT wafer was consistent with the theoretical values expected with both polymer structures. The consistently low actual values for chlorine were expected given its identity as a halogen counterion. The subsequent RAFT polymerization with METAC is further supported by the appearance of a nitrogen N1s peak at BE = 400 eV and chlorine peaks at BE = 268 eV and BE = 198 eV. If the pVL and pMETAC polymers are in a 1:1 ratio, the expected total bond type ratio would be 8 C-C bonds, 4 C-O bonds, 4 C-N bonds, and 2 C=O bonds. The obtained bond type percentages were 49.57% C-C, 17.56% C-O, 17.96% C-N, and 14.9% C=O, resulting in a ratio of 3.33:1.17:1.21:1, compared to the expected 4:2:2:1. The similarity in C-O and C-N bond type percentages on the surface are highly suggestive of a successful equally distributed mixed homopolymer brush.

Chapter 4

Conclusions and Outlook

A Y-shaped binary initiator allows for both ROP and RAFT polymerizations to be combined on one surface tethered initiator molecule, and thus more uniformly distributed along a surface. Moreover, multiple functionalities can be easily implemented on a surface from the two discrete methods of polymerization. The ROP/RAFT Y-shaped binary initiator was successfully synthesized via a ring-opening reaction of an epoxide. The reaction, energetically driven by the unfavorable steric crowding and ring strain, was carried out in a mild polar solvent at room temperature.

The experimental results indicate success of the synthesis of the binary initiator, the independent controlled polymerization methods of interest (RAFT and ROP), and the combination of these methods from the Y-shaped initiator molecule. Polymerization studies using the binary initiator were completed both in solution and on silicon oxide surfaces. Solution study products were analyzed and characterized via GPC and NMR, showing successful production of binary brushes regardless of the order in which the polymerizations were performed. The Y-shaped initiator was successfully immobilized on silicon oxide substrates and demonstrated to initiate RAFT and ROP polymerizations both individually and in sequence. The resulting polymer brushes were quantified and characterized via ellipsometry measurements and XPS analysis, with results supporting the production of advanced mixed polymer brush surface coatings.

Experimental

General material information

4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl] pentanol (CDTPA-OH), 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl] pentanoic acid (CDTPA), (3-

Glycidyloxypropyl)triethoxysilane, Nitromethane, δ -Valerolactone, 2,3,3-trimethyl indolenine, propane sultone, 2-hydroxy benzaldehyde. Zinc tetraphenylporphyrin (ZnTPP), 2,2'-azobis(2methylpropionitrile) (AIBN), dimethyl sulfoxide (DMSO), methyl methacrylate (MMA), [2-(Methacryloxy)ethyl]trimethylammonium chloride (METAC), ascorbic acid, triethyl amine (TEA) and ethyl acetate were purchased from Sigma-Aldrich and used as received. 5,6epoxyhexyltriethoxysilane was purchased from Gelest Inc. and used as received. Methylene chloride (DCM), hexanes, ethanol, toluene, and isopropanol were purchased from Fisher Scientific and used as received. Silicon wafers with native oxide were purchased from WaferPro, LLC (San Jose, CA). Collimated light-emitting diodes (LED's) were Thorlabs Olympus BX & IX series ($\lambda = 405$, 470, and 598 nm) were used for light-mediated reactions. The LED light intensities were modulated by a Thorlabs LED D1B T-cube driver.

General analytical information

Nuclear magnetic resonance (NMR) spectra were obtained using a Bruker AVIII-HD-500 MHz instrument. All ¹H NMR data is reported in parts per million (ppm) and normalized to the signal for the deuterated solvent CDCl₃ (7.26 ppm). Film thickness was measured with a J.A. Woolman RC2-D variable-angle spectroscopic ellipsometer (VASE) at 55°, 65°, and 75° incident angles with a wavelength range from 200 to 1000 nm. Optical constants and thicknesses were fit

using the CompleteEASE software package (J.A. Woollam Co., Inc.) with a three-layer model containing (a) bottom most silicon substrate layer, (b) 1.55-nm thick native silicon oxide layer, and (c) topmost polymer film layer. The polymer film layers were fit using a Cauchy model. X-ray photoelectron spectroscopy (XPS) measurements were perfumed using a Physical Electronics PHI VersaProbe II Spectrometer with a monochromatic Aluminum K_a X-ray source (1486.6 eV) under vacuum (10⁻⁸ Torr). Measurements were analyzed with CasaXPS software (Casa Software Ltd.).

Synthetic procedure for CDTPA-derived RAFT/ROP CTA

A 4 mL vial was charged with 4-Cyano-4-[(dodecylsulfanyl thiocarbonyl)sulfanyl]pentanol (195 mg, 0.5 mmol) and sparged for 10 minutes. Under nitrogen (3-Glycidyloxypropyl)triethoxysilane (270 μL, 0.3 mmol) and Nitromethane (600 μL) were added to the vessel before the reaction was stirred at room temperature (24 hrs). Upon completion, the reaction mixture was quenched with water and extracted using ethyl acetate before being dried over anhydrous sodium sulfate. The reaction mixture was then decanted and filtered before being concentrated in vacuo. Column chromatography (7 hexanes: 3 EtOAc) was used to purify the reaction mixture yielding the title compound, a viscous oily yellow liquid. ¹H NMR (500 MHz, CDCl₃, 25 °C, ppm): 0.632-0.704 (t, 2H), 0.846-0.941 (t, 8H), 1.254-1.436 (m, 46H), 1.811-1.934 (m, 9H), 2.086-2.167 (m, 2H), 2.257-2.342 (m, 2H), 3.178-3.250 (t, 1H), 3.306-3.397 (t, 4H), 3.449-3.511 (t, 2H), 3.530-3.572 (d, 1H), 3.572-3.668 (m, 2H), 3.691-3.773 (m, 4H), 3.795-3.909 (q, 5H).

General procedures for ROP polymerization in solution

The photocatalytic acid was weighed out in a vial and stored in the dark. The Y-shaped binary initiator, monomer and photocatalyst were combined with a molar ratio of [Monomer]:[Photocatalyst]:[Initiator] = 50:0.25:1 and 1 mL of tetrahydrofuran (THF). The mixture was then sparged with nitrogen for 20 minutes. The reaction mixture was irradiated with a blue LED light at an intensity of 150 a.u. for ten hours. The polymerization was terminated by the addition of TEA. The polymer was precipitated in cooled methanol and filtered before being dried in vacuo.

Binary CTA functionalized surface

Silicon substrates with native oxide layer were cut into 1 x 1 cm squares before being cleaned by sonication in toluene (10 min) followed by sonication in isopropanol (10 min), and then dried with nitrogen gas. The wafers were then cleaned and activated by a plasma cleaner (PDC-001, Harrick Plasma) under 300 mTorr (15 min). After cleaning, the wafers were placed, non-overlapping, in a petri dish before being covered with a solution containing 20 μ L of synthesized CTA (Compound 1) in 40 mL of dry toluene for 48 hours. When complete, the functionalized substrates were rinsed with toluene, isopropanol, dried under a stream of nitrogen gas and stored under nitrogen.

General procedures for RAFT polymerization on the surface

All light mediated reactions were placed approximately 1.5 cm below an LED light source in a fume hood set up. A stock solution of 1 mg photocatalyst (ZnTPP) in 1mL DMSO or water was prepared in a vial and stored in the dark. Monomers containing inhibitors were purified through a basic alumina column to remove inhibitor prior to use. Unless otherwise noted, the monomer and photocatalyst were mixed in a 4 mL vial with a molar ratio of [Monomer]:[Photocatalyst] = 500:1. A binary CTA-functionalized silicon wafer was placed on a glass slide before the reaction mixture was pipetted onto the wafer and covered with a glass coverslip. A resulting uniformly thin layer of solution between the coverslip and wafer was then irradiated with LED light at an intensity of $1.1 \ \mu$ W/cm² for a predetermined time. Upon completion of irradiation, the wafers were rinsed with DCM or water and dried with nitrogen gas.

General procedures for ROP polymerization on the surface

All reactions were placed approximately 1.5 cm below an LED light source in a glove box set up. The photocatalytic acid was weighed out in a vial and stored in the dark. Unless otherwise noted, the monomer and photocatalyst were mixed in a 4 mL vial with a molar ratio of [Monomer]:[Photocatalyst] = 500:1. The mixture was then sparged and transferred to a nitrogenous atmosphere. A binary CTA-functionalized silicon wafer was placed on a glass slide before the reaction mixture was pipetted onto the wafer and covered with a glass coverslip. A resulting uniformly thin layer of solution between the coverslip and wafer was then irradiated with 407 nm LED light at an intensity of $1.1 \ \mu$ W/cm² for a predetermined time. Upon completion of irradiation, the wafers were rinsed with THF and dried with nitrogen gas.

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ACADEMIC VITA

DEVON M. SWEEDER

dms680@psu.edu

Education	The Pennsylvania State University, University Park, PA BS in Chemistry, minor in Global Health (Honors in Chemistry, The Schreyer Honors College)	May 2022
Experience	Undergraduate Research Assistant Dr. Christian Pester, The Pennsylvania State University	
	Dr. Sheryl Dykstra	
	Undergraduate Research Assistant Dr. Richard Ordway, The Pennsylvania State University	
Publications	Superhydrophilic Polymer Brushes with High Durability and Anti-fogging Activity <i>ACS Applied Polymer Materials</i> 2021, 3(10)	
	Genetic Analysis of the Drosophila ESCRT-III complex protein, VPS24, reveals a novel function in lysosome homeostasis <i>PLoS ONE</i> 2021. 16(5)	
Awards and	John and Elizabeth Holmes Teas Scholarship	2019- Present
Grants	Stephen and Patricia Benkovic Summer Research Award Dean's List	2021 2018- Present
Professional Organizations	Penn State Hershey Children's Hospital - Volunteer Global Medical Brigades at Penn State - Treasurer Susquehanna Service Dogs – Puppy Raiser	2019- Present 2020- Present 2016- 2019