# Polymer Brush Growth by Surface-initiated Ring-opening Polymerization from a Cross-linked Polymer Thin Film

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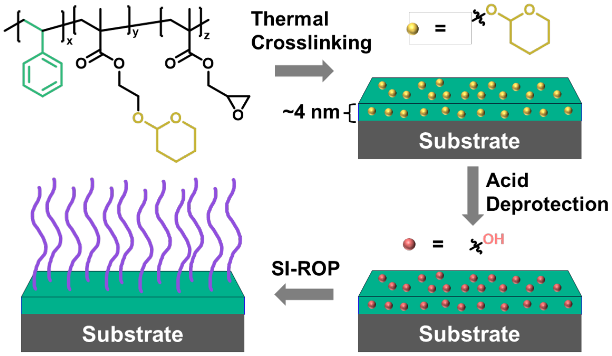


# ABSTRACT

Modification of a surface with polymer brushes has emerged as an effective approach to tune the properties of a substrate. Brushes grown from an inimer-containing cross-linkable polymer coating provide significant advantages compared to other “grafting-from” methods, such as improved stability, increased grafting density, and the potential to control the grafting density. So far, the inimer coating method has only been applied for surface-initiated controlled radical polymerizations. In this work, we present an approach for the fabrication of a stable cross-linked ultra-thin polymer coating containing hydroxyl groups which serve as initiating sites for surface-initiated ring-opening polymerization (SI-ROP). The polymers used for the fabrication of the coatings consist of 2-((tetrahydro-*2H*-pyran-2-yl)oxy)ethyl methacrylate (THPEMA), a small fraction of a cross-linkable unit, and a diluent styrene. Three coatings with varying THPEMA and styrene content were fabricated, and poly(dimethyl siloxane) (PDMS) and poly(caprolactone) (PCL) brushes were grown by SI-ROP of hexamethylcyclotrisiloxane ($D_3$), and ε-caprolactone respectively The brushes were characterized by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), static contact angle measurements, ellipsometry and size exclusion chromatography (SEC). The results demonstrate a well-controlled ROP of $D_3$ and ability to control grafting density by tuning the THPEMA content of the coatings.

## 1. INTRODUCTION

Surface modification with polymer brushes[1] has been used as an effective means for tuning the interfacial properties of planar surfaces, nanoparticles, and biobased materials such as cellulose.[2] The properties of the brushes are greatly influenced by their grafting density, which dictates their conformation.[3] Densely grafted chains in the "brush" regime typically adopt a stretched conformation, while brushes with low grafting density in the "mushroom" regime adopt a random coil configuration.[4-5] Synthesis of these brushes by "grafting-to" method of anchoring reactive end-group of a preformed polymer chain to an appropriate substrate allows for full characterization of the polymer brushes but is limited to relatively low grafting densities. Because of this, "grafting-from" method consisting of growing the polymer chains from initiating groups anchored to the surface is often preferred as it allows for higher grafting densities and thicker polymer films.[6]

For the "grafting-from" method to generate high grafting density brushes, a general approach has been to anchor initiating sites to the substrate through the formation of a self-assembled monolayer (SAM). Following this approach, polymer brushes from vinylic monomers have been synthesized by surface-initiated atom-transfer radical polymerization (SI-ATRP), nitroxide mediated polymerization (SI-NMP), reversible addition-fragmentation chain transfer (SI-RAFT), and ring-opening metathesis polymerization (SI-ROMP).[5, 7-12] While SAMs have been effective for growing polymer brushes, they have limited stability towards various reagents, and are limited by substrate-dependent anchoring chemistry.[6] To overcome these limitations, we have developed a simple approach for anchoring ATRP, NMP and/or RAFT initiators using an inimer-containing cross-linkable polymer coating.[13-15] The polymer coatings developed for this approach consist of an inimer and a small fraction of cross-linkable methacrylate that can form a stable crosslinked thin film upon thermal annealing.[16] Furthermore, by incorporating a third comonomer that lacks reactive functional groups, such as styrene, control over the grafting density of the brushes can be achieved by tuning the inimer: styrene ratio.[13] The thickness of these coatings can be as low as 2 nm to promote a monolayer brush growth mimicking growth from a traditional SAM.[15]

Expanding the scope of this chemistry to include non-vinyl monomers such as those that can be polymerized by ring-opening polymerization (ROP) is highly desirable for the facile growth of polyesters such as polycaprolactone (PCL),[17-19] polypeptides,[20-21] and polysiloxanes such as polydimethylsiloxane (PDMS).[22] These polymer brushes have found applications in a wide variety of fields including medicine, drug delivery, solid polymer electrolytes, and others.[21-25] PDMS brushes in particular have garnered significant attention due to their low surface energy, liquid-like properties, good chemical and thermal stability, and biocompatibility.[26] As a result, PDMS brushes have found applications as super-liquid repellent surfaces and slippery surfaces with excellent antifouling properties.[27] Similarly, due to their biocompatibility, biodegradability, and hydrophobicity, PCL brushes have been widely used to improve the compatibility of cellulosic materials in non-polar matrices[28-29] and as degradable polymer brush coatings for biomedical applications.[30-31]

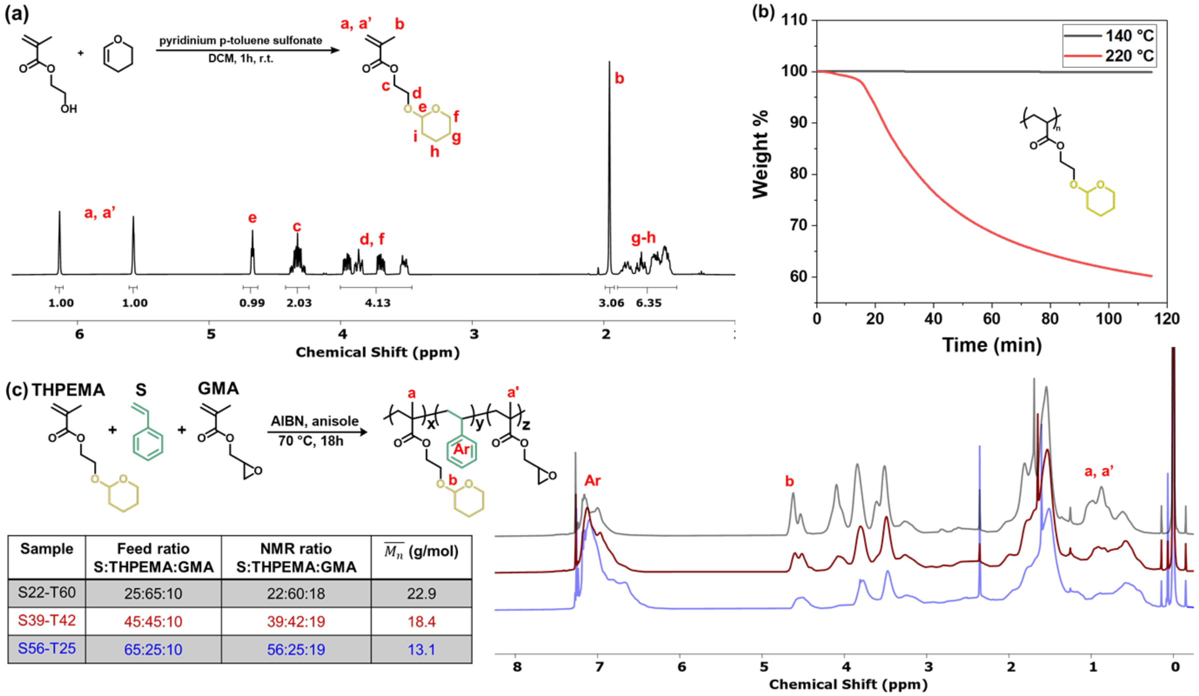
Unlike surface-initiated polymerization of vinyl monomers, which often require surface modification to anchor initiating sites, many substrates naturally possess hydroxy groups on their surfaces, making them suitable for SI-ROP without additional treatment. For example, the SI-ROP of ε-caprolactone to yield PCL brushes using the surface hydroxyl groups of cellulose as initiators has been used as an effective method for the modification of cellulosic structures.[17-19] Additionally, PDMS brushes are typically synthesized from hydroxy groups on the surface of silicon substrates.[26, 32] For substrates that require surface modification, a general approach for immobilizing the hydroxyl or amine initiators needed for SI-ROP involves the formation of SAMs.[55,33-35]

In this work, we present an approach for the incorporation of an ROP inimer into a cross-linkable polymer coating. Since hydroxyl groups are commonly used as initiators in ROP, we chose to incorporate 2-((tetrahydro-*2H*-pyran-2-yl)oxy)ethyl methacrylate (THPEMA) monomer as the ROP inimer. Tetrahydropyranyl ether (THP) protection was required to avoid crosslinking of the hydroxyl groups with the substrate during thermal annealing. Thus, random copolymers of THPEMA, styrene, and glycidyl methacrylate (GMA) were synthesized and used to fabricate coatings on silicon and gold substrates. After thermal annealing, stable crosslinked thin films were obtained, that were then exposed to mild acidic conditions to induce the THP deprotection reaction. PDMS and PCL brushes were prepared by the organocatalytic SI-ROP of hexamethylcyclotrisiloxane ($D_3$) and ε-caprolactone, respectively, using the hydroxyl groups of (hydroxyethyl)methacrylate (HEMA) in the coating as initiating sites. This approach allows for the tuning of the brush grafting density by adjusting the THPEMA content in the random copolymer used to fabricate the inimer coating. Characterization by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), ellipsometry and static contact angle measurements demonstrated good control over grafting density. Furthermore, the size exclusion chromatography (SEC) and end group analysis by proton nuclear magnetic resonance ($^1$H-NMR) spectroscopy of PDMS and PCL grown from free initiator added to the reaction mixture during brush growth shows a well-controlled ROP of $D_3$ and ε-caprolactone, respectively.

## 2. RESULTS AND DISCUSSION

### 2.1 Synthesis of THPEMA random copolymers

One of the major advantages of the inimer coating approach for surface-initiated brush growth is the formation of a stable thin film on a wide variety of substrates, such as oxides, gold, glass, and III-V's.[14-15, 36] The incorporation of GMA into the random copolymer results in a crosslinked coating that has shown to be stable in organic solvents under ultrasonication conditions.[14-16] GMA is an epoxide-containing self-crosslinkable unit that can be cross-linked upon thermal annealing at 120 °C. For ROP initiator hydroxyl groups are required in the coating. Since free hydroxyl groups can ring open epoxy, as well as crosslink to the substrate at elevated temperatures by ether bond formation, a THP protected HEMA was used as a comonomer with GMA (Figure 1a). THP was chosen as the protecting group due to its thermal stability and its deprotection under mild acidic conditions.



| Sample | Feed ratio S:THPEMA:GMA | NMR ratio S:THPEMA:GMA | $\overline{M_n}$ (g/mol) |
|---|---|---|---|
| S22-T60 | 25:65:10 | 22:60:18 | 22.9 |
| S39-T42 | 45:45:10 | 39:42:19 | 18.4 |
| S56-T25 | 65:25:10 | 56:25:19 | 13.1 |

**Figure 1.** a) Synthesis and $^1$H-NMR spectrum of THPEMA, b) Isothermal TGA experiment of a THPEMA homopolymer, and c) Synthesis and $^1$H-NMR spectra of random copolymer library of THPEMA, GMA, and styrene.

The thermal stability of the THP group was assessed by thermogravimetric analysis (TGA) of a THPEMA homopolymer synthesized by ATRP. The THPEMA homopolymer showed a 2-stage decomposition starting at 215 °C (**Figure S1**). The weight loss in the first stage was 61.9%, corresponding to the loss of the THP group. The second stage of decomposition showed a 31.6% weight loss corresponding to the decomposition of the remaining pendant groups and backbone. An isothermal TGA experiment at 220 °C for 2 hours was performed and a weight loss of ~40% was observed, confirming that the first stage decomposition corresponds to the loss of the THP (**Figure 1b**). To further assess the stability of the THP group, an isothermal TGA experiment was performed at 140 °C for 2 hours (**Figure 1b**). As there was no observable weight loss during the isothermal scan, the THP group was confirmed to be stable at a temperature typically used to crosslink the GMA in the coating.

By incorporating a third non-reactive comonomer such as styrene in the copolymer the grafting density of the brushes can be readily tuned. Thus, three random copolymers of THPEMA, GMA, and styrene with a fixed GMA ~ 10 mole % and varying ratio of styrene to THPEMA were synthesized (Figure 1c). The random copolymers were labeled as "S*A*-T*B*", where *A* and *B* are the mole percent of styrene and THPEMA, respectively, as determined by $^1$H-NMR analysis. The final polymer compositions of all random copolymers showed a higher incorporation of GMA compared to the feed. The experimentally determined reactivity ratios for THPEMA and GMA (**Figures S2**) reveal an ideal copolymerization with a truly random distribution ($r_{GMA} = 1.014$ and $r_{THPEMA}= 0.999$). Reactivity ratios determined for the copolymerization of THPEMA and styrene (**Figure S3**) ($r_{styrene} = 0.738$ and $r_{THPEMA}= 0.587$) show their tendency for a statistical copolymer. GMA is known to have a higher reactivity in free radical polymerization conditions compared to styrene.[37] Taken together the higher incorporation of GMA in the copolymers seems reasonable.

The $^1$H-NMR spectra of the random copolymers shown in Figure 1c reveal an upfield shift and splitting of the THPEMA peak at ~4.6 ppm as the styrene composition increases. This is likely due to interactions between the THP pyranyl ether and the phenyl of styrene, as the splitting is not observed in the $^1$H-NMR spectra of the THPEMA homopolymer or THPEMA and GMA random copolymers (**Figure S4**). The number average molecular weight ($\overline{M_n}$) of the random copolymers (**Figure 1c**) obtained by SEC correspond to a degree of polymerization (DP) of 94.3, 116.7, and 129.3, for S56-T25, S39-T42, and S22-T60, respectively. The increase in DP correlates with the decrease in the amount of the less reactive styrene monomer in the feed.

### 2.2 Fabrication of the ROP inimer coating

The fabrication of the inimer coating is depicted in **Figure 2a**. First, S22-T60 was used to study crosslinking efficiency of the random copolymers containing the ROP inimer at 120, 130, and 140 °C as THPEMA was found to be stable in this temperature range. A 0.3 w/w % solution in toluene of the S22-T60 random copolymer was spin coated onto piranha treated silicon wafers to yield ~8 nm thick films. The substrates were then heated under vacuum, rinsed with toluene to remove uncrosslinked polymer and air-dried. The resulting thickness was measured by ellipsometry. The as-spun coated thickness was chosen as the reference to normalize thicknesses after thermal cross-linking and toluene rinse. As shown in **Figure 2b**, the normalized thickness increased with both temperature and time, plateauing at around 0.8. These results align well with our previous studies on GMA-containing random copolymers,[14-15] showing the self-crosslinkable nature of the epoxy units and covalent attachment to the surface hydroxyl groups upon heating. In all further studies 130 °C/30 min was used to cross-link the inimer coatings as it allowed for the formation of a sufficiently thick coating (~4.5 nm) at relatively short annealing times.

The stability of the inimer coating after thermal annealing was further assessed by measuring its thickness and contact angle before and after sonicating for 20 minutes in toluene (**Table S1**). A slight decrease in the thickness of the inimer coating from (4.48 ± 0.04) nm to (3.87 ± 0.14) nm was observed, probably due to the loss of uncrosslinked entangled chains upon sonication. The static water contact angle of the substrates remained unchanged after sonication, confirming the retention of the inimer coating. Overall, these results demonstrate the stability of the coating.

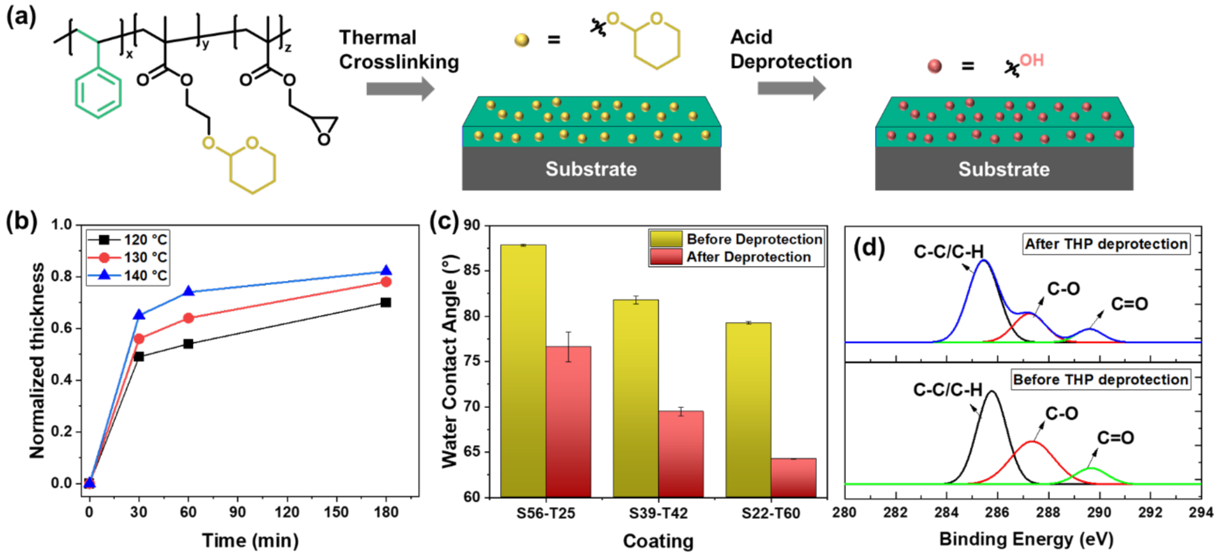


**Figure 2.** a) Schematic representation of the structure and fabrication of the inimer coatings used for brush growth. b) Plot of the normalized thickness as a function of time at different temperatures for S22-T60. c) Static water contact angle measurements before and after deprotection for the inimer coatings. d) 1Cs XPS spectra of the S22-T60 inimer coating before and after deprotection.

The deprotection of the inimer coating was performed by dipping the substrates on a 0.1M HCl solution of tetrahydrofuran (THF): ethanol (2:1). Before deprotection, the water contact angles of the coatings decreased as the hydrophobic styrene content decreases. Post deprotection, the contact angle decreases due to the hydrophilicity of the exposed hydroxyl groups. As expected, a larger decrease in the contact angle was observed as the THPEMA content increased, corresponding to a larger amount of hydroxyl groups. After deprotection, a similar thickness of ~4 nm was obtained for all inimer coatings (**Table S2**).

Further characterization of the inimer coatings by XPS is shown in **Figure 2d**. High-resolution C1s peaks were deconvoluted and analyzed to track the surface compositional changes due to the deposition and deprotection of the inimer coatings. Only the XPS spectra of the S22-T60 is shown to compare the differences before and after deprotection, as similar trends were observed for two other coatings (**Figure S5)**. The differences in the composition of the coatings are directly reflected in the intensities of the C-O peak at 287.8 eV, with higher intensities observed for S22-T60 both before and after THP deprotection **(FigureS5)**. The total C1s peak area ($A_{C1s}$) and deconvoluted C-O peak area ($A_{C\text{-}O}$) of the three inimer coatings were calculated (**Table S3**). The $A_{C\text{-}O}/A_{C1s}$ ratio before and after THP deprotection increases with increasing content of THPEMA in the coatings. After deprotection, a reduction in the $A_{C1s}$ and $A_{C\text{-}O}$ for all three coatings, confirmed the loss of the THP groups. This decrease was particularly pronounced in S22-T60, attributable to its higher THPEMA content. Overall, these results confirm that the THP deprotection of the inimer coatings was successful.

### 2.3 Brush growth by organocatalytic ROP

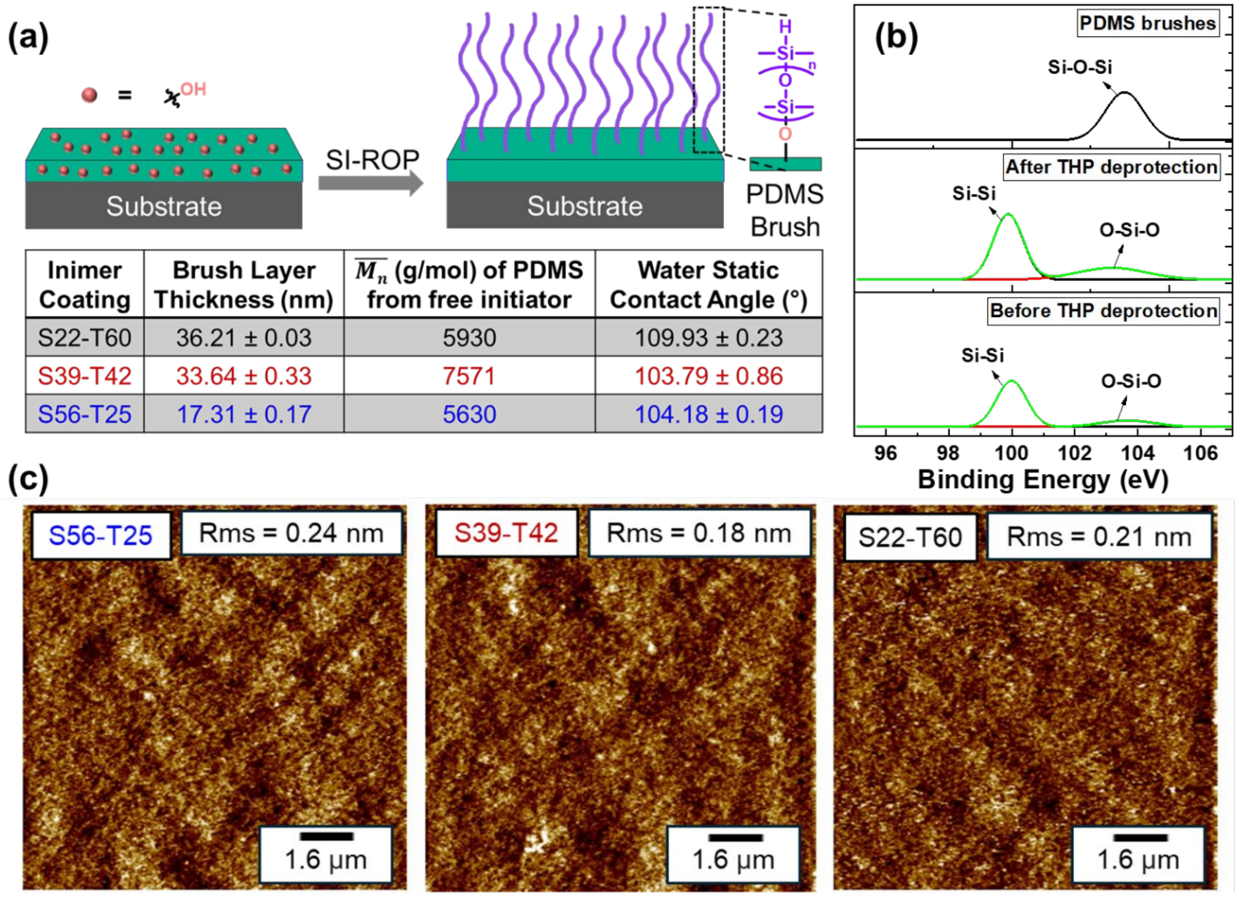
PDMS brushes were grown from the inimer coatings by organocatalytic ROP of $D_3$ from all three coatings under identical reaction conditions (**Figure 3a**). Water was added to the brush growth solutions as a free initiator to control the polymerization.

The thickness of the PDMS brush layers measured increased from ~17 nm to 36 nm as the THPEMA content in the coating increases from 25 to 60% (**Figure 3a**). Since the three inimer coatings were subjected to the same brush growth conditions, the molecular weight (MW) of the resulting brushes should be similar. In fact, PDMS grown from free initiator in the brush growth solutions show an identical SEC trace for S56-T25 and S22-T60, and a slightly higher MW trace for S39-T42 (**Figure S7**). This is confirmed by $^1$H-NMR end group analysis of the PDMS grown from sacrificial initiators showing a similar MW for S56-T25 and S22-T60 and a higher MW for S39-T42 (**Figure 3a** and **Figure S8**). Despite a similar MW for the PDMS chains grown from free initiator in the brush growth solution, the thickness of the surface grown brushes from S22-T60 was double that of S56-T25. Thus, these results demonstrate that the differences in the thickness of the PDMS brush layers correspond to the extended conformation adopted by the chains at higher grafting densities.

The contact angles measured for S56-T25, S39-T42, and S22-T60 after brush growth were 104.18 ± 0.19°, 103.79 ± 0.86°, and 109.93 ± 0.23° respectively (**Figure 3a**), which agrees well with previous reports on PDMS brushes.[25-26, 38-39] The conformation of the PDMS brushes can have a significant impact on the contact angle,[40] thus, the 5-6° difference in contact angle between S22-T60 and the other two coatings is likely a direct result of the highly stretched conformation adopted by the brushes at this highest grafting density.

High resolution Si2p peaks were deconvoluted and analyzed to track the compositional changes due to PDMS brush growth by XPS (**Figure 3b**, **Figure S6**). The high resolution Si2p spectra for the S22-T60 inimer coatings before and after deprotection shows a Si-Si peak at ~99.95 eV and the O-Si-O peak at ~103.22 eV due to the elemental silicon and silicon oxide layer from the substrate. After PDMS brush growth, a single peak at ~103.59 eV corresponding to the Si-O-Si bond from the PDMS backbone was observed. C1s spectra confirmed absence of any C=O and C-O peaks from the coating after brush growth as the brush thickness was well above the mean escape depth (10 nm) of XPS (**Figure S5**). Instead, a C-Si peak at ~286.05 eV was observed from the PDMS brush, confirming the successful SI-ROP of PDMS brushes.

A very low roughness of 0.24 nm, 0.19, and 0.21 nm was measured by AFM for PDMS brushes grown from S56-T25, S39-T42, and S22-T60 respectively (**Figure 3c)**. These results, along with the narrow dispersity obtained for the PDMS grown in solution (**Figure S7**) confirm a remarkably homogenous growth of PDMS brushes. Similar roughness values have been reported for PDMS brushes prepared by a polycondensation reaction using a grafting-from approach for very low brush thicknesses of <5nm.[26, 32] PDMS brushes grown by our method have 6 times higher thickness and still maintain a very low roughness, hence the polymerization process developed here is well controlled.



| Inimer Coating | Brush Layer Thickness (nm) | $\overline{M_n}$ (g/mol) of PDMS from free initiator | Water Static Contact Angle (°) |
|---|---|---|---|
| S22-T60 | 36.21 ± 0.03 | 5930 | 109.93 ± 0.23 |
| S39-T42 | 33.64 ± 0.33 | 7571 | 103.79 ± 0.86 |
| S56-T25 | 17.31 ± 0.17 | 5630 | 104.18 ± 0.19 |

**Figure 3**. a) Schematic representation of PDMS brush growth by SI-ROP. The PDMS brush layer thickness, static water contact angle, and $\overline{M_n}$ of the PDMS grown in solution for inimer coatings is presented. $\overline{M_n}$ was calculated by $^1$H-NMR end group analysis. b) High resolution Si2p XPS spectra for PDMS brushes grown on S22-T60 inimer coating. c) AFM height images of PDMS brushes grown from the inimer coatings.

For calculation of grafting density of the PDMS brushes using the equation below, the $\overline{M_n}$ of the PDMS chains is required:

$$\sigma = hN_{av}\rho/\overline{M_n}$$

where $\sigma$ is the grafting density, $h$ is the thickness of the brush layer, and $\rho$ is the bulk density of PDMS. Typically, the $\overline{M_n}$ of the chains grown from the free initiator in the brush growth solution are assumed to be a close approximation for brushes grown from the solution. Alternatively, the brushes can be cleaved from the surface and the $\overline{M_n}$ can be directly measured by SEC. In our system due to lack of an appropriate cleaving technique, and the measured thickness of the PDMS brushes far exceeding the contour length of the PDMS grown from free initiator (**Table S4**), the molecular weight for the surface grown brushes is likely much higher compared to the solution grown PDMS. Due to this discrepancy, the grafting density of the brushes could not be calculated. Nevertheless, kinetic studies using the S22-T60 inimer coating showed direct correlation between the thickness of the PDMS brush layer and the $\overline{M_n}$ of the PDMS grown from free initiator in solution (**Figure S9a and b**). Both thickness and molecular weight increase with time and plateaus at around 120 minutes. At this point, SEC analysis of the PDMS grown from free initiator showed an increase in Đ (**Figure S9a**). These results suggest that after two hours, the monomer is mostly depleted and there is potentially coupling between propagating PDMS chains. This is evidenced by the higher MW shoulder in the SEC trace at 240 minutes of brush growth (**Figure S9c**).

We also tested the efficacy of the inimer coating for SI-ROP of ε-caprolactone. Organocatalytic ROP of ε-caprolactone from all three coatings were conducted under identical reaction conditions to create PCL brushes (**Figure S10a**). 1-pyrenebutanol was added to the brush growth solutions as a free initiator to control the polymerization and enable end-group analysis by

NMR. Similar to studies on the growth of PDMS brushes, PCL brushes with increasing thickness from 21 to 40 nm were achieved as the THPEMA content increased in the coating. The MW of the PCL grown from free initiator were similar in all brush growth solutions, evidenced by both $^1$H-NMR end group analysis and SEC (**Figure S10b and S11**). Hence, the increased thickness is attributable to the increase in grafting density of the brushes, resulting in stretched conformation. Interestingly, similar to the PDMS brushes, the thickness of the PCL brushes grown from S22-T60 was nearly double that from S56-T25. Measured static water contact angles for the PCL brushes were in good agreement with those previously reported for PCL brushes.[30-31] The deconvoluted high resolution C1s and O1s XPS spectra (**Figure S12**) of the PCL brushes showed the expected characteristic peaks for C-C ~286.2 eV, a C-O ~287.8 eV, C=O~290.1 eV, O-C ~533.4 eV and a O=C~534.8 eV.

As with the PDMS brushes, the thickness of the PCL brushes exceeded the contour length of the PCL grown from free initiator in the brush growth solutions (**Table S5**), though to a lesser extent. It is known in the literature that there are discrepancies in the molecular weight of brushes from that of the polymers in the brush growth solution, but the reasons are less apparent. In many cases[6] the surface grown brushes have a lower MW compared to free chains due to limited diffusion of the monomers to the surface initiating sites. However, there are other reports where the opposite effect is reported, attributable to modification of specific kinetic parameters due to surface confinement especially for high density polymer brushes[15, 41-42]. Overall, these results demonstrate that the grafting density of the PDMS or PCL chains grown from the ROP inimer coatings can be tuned by varying the THPEMA content in the random copolymers. The narrow Đ observed for the PDMS/ PCL grown from the sacrificial initiator confirms a well-controlled ROP.

To demonstrate the generalizability of this strategy to substrates other than silicon, we deposited the S22-T60 coating on a gold coated silicon substrate and conducted SI-ROP of both $D_3$ and ε-caprolactone. Successful PDMS and PCL brush growth was observed in both cases (**Figure S13**), confirming the substrate independent nature of this chemistry.

## 3. CONCLUSIONS

This study presents an effective approach for the incorporation of a ROP inimer into a cross-linkable polymer coating that can be applied on all types of substrates. This was enabled by the THP protection of HEMA, which affords a thermally stable group that can be deprotected under mild acidic conditions to present hydroxyl groups from the coating to initiate ROP. Polymerization of $D_3$ and ε-caprolactone was chosen as a test case to evaluate the efficacy of the inimer coating in SI-ROP. Characterization of the PDMS and PCL brushes reveals a well-controlled ROP, along with effective control of the thickness and conformation of the brushes. Compared to other approaches for SI-ROP, this method allows for rational tuning of the grafting density by controlling the THPEMA composition of the coatings. The ability to characterize the copolymer composition precisely before its deposition to the substrate, and its applicability to non-oxide substrates by simple spin coating and crosslinking, make this methodology a valuable tool for polymer brush growth of non-vinyl monomers.

## 4. METHODOLOGY

### Materials

Hexamethylcyclotrisiloxane ($D_3$) was purchased from Fisher. ε-caprolactone was purchased from TCI Chemicals. All other solvents and reagents were purchased from Sigma-Aldrich Chemical

Co. (Milwaukee, WI) and used without further purification unless otherwise specified. $D_3$, ε-caprolactone , styrene and GMA were stirred over calcium hydride, distilled under reduced pressure and stored under Ar gas in the fridge. (TMnPG) was synthesized according to a procedure reported on the literature.[43] Tetrahydrofuran (THF) was freshly purified by solvent towers purchased from VAC. Si (100) wafers were test grade wafers purchased from UniversityWafer, Inc. Gold-coated glass slides (Ti 5 nm, Au 100 nm) were purchased from EMF Corporation.

**Synthesis of 2-((tetrahydro-*2H*-pyran-2-yl)oxy)ethyl methacrylate THPEMA**

A solution of HEMA (9.32 mL, 76.84 mmol) in DCM (100mL) was prepared on a 500 mL round bottom flask. After purging with Ar gas for 15 minutes, 3,4-Dihydro-2H-pyran (9.82 mL, 107.6 mmol) and pyridinium p-toluene sulfonate (0.1042 g, 0.42 mmol) were added to the flask. The reaction mixture was stirred at room temperature and monitored by TLC until full conversion was reached, after approximately 3 hours. A saturated solution of sodium bicarbonate (100 mL) was then added to the reaction mixture and transferred to an extraction funnel. After washing 3 times with a saturated solution of sodium bicarbonate and once with DI water, the organic phase was dried over magnesium sulfate and filtered. DCM was then removed by rotary evaporation and the crude product was further purified by flash column chromatography using silica gel and a mixture of 4:1 hexane to ethyl acetate. Excess solvent was removed by rotary evaporation followed by drying under vacuum. The resulting clear viscous liquid (94% yield) was purged with Ar gas and stored in a freezer until further use. $^1H$ NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 6.1$ (s, 1 H; CH2), 5.6 (s, 1 H; CH2), 4.7 ppm (t, 3J(H,H) = 3.6 Hz, 1 H; CH), 4.3 ppm (m, 2 H; CH3), 3.95 ppm (m, 1 H; CH2), 3.86 ppm (m, 1 H; CH2), 3.7 ppm (m, 1 H; CH2), 3.5 ppm (m, 1 H; CH2), 3.7 ppm (m, 1 H; CH2), 3.5 ppm (m, 1 H; CH2), 1.96 ppm (s, 3 H; CH3), 1.82 ppm (m, 2H; CH2), 1.71 ppm (m, 2H; CH2), 1.6 ppm (m, 2H; CH2), 1.54 ppm (m, 2H; CH2).

## General Procedure for the Synthesis of Random Copolymers

The random copolymers were synthesized by conventional free radical polymerization according to this general procedure. In a 25 mL Schlenk flask equipped with a magnetic stir bar, THPEMA (2.0 g, 2.33 mmol), styrene (0.41 mL, 3.59 mmol), GMA (0.20 mL, 1.44 mmol), and AIBN ( 0.024 g, 0.14 mmol) were dissolved in anisole (10 mL). The reaction mixture was degassed by three cycles of freeze-pump-thaw, and the flask was then filled with Ar gas and placed in an oil bath at 70°C. After 16 hours, the reaction mixture was cooled and precipitated in methanol 3 times. The resulting white powder was collected by filtration and dried overnight on a vacuum oven. The random copolymers were stored in a freezer until further use.

## General Procedure for the Formation of the Inimer Coating and Deprotection of the THP Group

2x1 cm$^2$ Si (100) wafers cleaned with a piranha solution ($H_2SO_4$:$H_2O_2$ = 3:1, highly explosive when in contact with organics) were spin coated (4,000 rpm, 3,000 r/s, 30 s) using a 0.3 wt% solution of a p(S-*r*-THPEMA-*r*-GMA) copolymer on toluene. The wafers were subsequently thermally annealed at 130°C for 30 minutes to induce the crosslinking of GMA. The wafers were then dipped in toluene for 20 minutes and rinsed with copious amounts of toluene to remove uncrosslinked random copolymer. Afterwards, the wafers were air dried and stored under vacuum until further use.

The deprotection reaction of the inimer coating was performed according to the following procedure. The wafer was placed on a 20 mL glass vial. THF (2 mL), EtOH (1 mL), and a 1.2 M HCl solution (0.25 mL) were added, and the flask was placed on an orbital shaker overnight. The wafers were then soaked in THF and washed with copious amounts of THF and DI water. The wafers were air dried and stored under vacuum until further use.

### General Procedure for PDMS Brush Growth

PDMS brushes were grown following an organocatalytic ROP procedure modified from the literature.[43] A Si wafer containing a deprotected inimer coating was placed on a 20 mL glass vial and sealed with a rubber septum. After purging with Ar gas, 2 mL of a 0.5 g/mL solution of $D_3$ in DCM:THF (5:1) containing 1.8 μL of DI water were added. Subsequently, 0.5 mL of a 10 mg/mL solution of TMnPG in DCM:THF (5:1) were added and the vial was placed on an orbital shaker. After 1 hour, the polymerization was terminated by adding 25 μL of chlorodimethylsilane and 29 μL of pyridine. The wafers were then soaked in THF, rinsed with THF and DI water and air dried. The brush growth solution was dumped in acetonitrile and PDMS grown from free initiator was precipitated. The recovered PDMS was dried in a vacuum oven overnight and characterized by SEC and NMR.

### General Procedure for PCL Brush Growth

PCL brushes were grown following an organocatalytic ROP procedure modified from the literature.[44] ε-caprolactone (2.5 g, 22 mmol) and 1-pyrenebutanol (0.109 g, 0.4 mmol) were dissolved in anhydrous benzene (8 mL). A second solution of TBD (13.9 mg, 0.1 mmol) in benzene (2 mL) was prepared. 2x1 $cm^2$ Si wafer containing a deprotected inimer coating was placed on a dried and degassed 20 mL glass and sealed with a rubber septum. 2 mL of the monomer solution and 0.5 mL of the TBD solution were then added to the vial. The vial was then placed in an orbital shaker for 5 hours at room temperature. The Si wafer was then taken out of the reaction mixture, soaked in toluene, rinsed with copious amounts of toluene, and air dried. The brush growth solution was dumped in hexane and PCL grown from free initiator was precipitated. The recovered PCL was dried in a vacuum oven overnight and characterized by SEC and NMR.

**Characterization**

Size Exclusion Chromatography (SEC) was performed using a Viscotek 2210 system equipped with three Waters columns (HR4, HR 4E, and HR3). THF was used as the eluent with a flow rate of 1 mL/min at 30 °C. The calibration curve for analysis consisted of nine narrow dispersity PS standards with $\bar{M}_n$ from 1 to 400 kg/mol. All NMR spectra were recorded in $CDCl_3$ using a Bruker Avance-400 spectrometer. TGA was carried out with a TA Instruments Q500 using a heating rate of 10 °C/min under a nitrogen atmosphere. The inimer coating thickness was measured using a Semilab SE-1000 spectroscopic ellipsometer at a wavelength range of 350-990 nm. Three different spots within the same substrate were measured and the reported thickness corresponds to the average of those measurements. X-ray photoelectron spectroscopy (XPS) was done using a Thermo K-alpha XPS with a 400 $\mu m^2$ probing area and monochromatic Al Kα radiation (1486.7 eV). The survey spectra and high-resolution spectra were acquired using analyzer pass energies of 200 and 50 eV, respectively. Data was analyzed using the Avantage XPS software package. To make the XPS peaks more visible, XPS data was subtracted from the background signal and baseline adjusted. The common C-C/C-H peak is used as a reference peak where heights of all other peaks were scaled relative to the height of the reference peak by dividing the entire data points with the maximum intensity of the reference peak. Atomic force microscopy (AFM) images were acquired using a Bruker Dimension Icon with TESPAV2 probe tips in the tapping mode. Contact angle measurements with DI water were done using a Dataphysics OCA 15 plus Contact Angle measuring device with SCA 20 software. Three different spots within the same substrate were measured and the reported static contact angle corresponds to the average of those measurements.

## SUPPORTING INFORMATION

Supporting Information is available from the Wiley Online Library or from the author.

## ACKNOWLEDGEMENTS

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## CONFLICT OF INTEREST

The authors declare no conflict of interest.

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# Supporting Information

# Polymer Brush Growth by Surface-initiated Ring-opening Polymerization from a Cross-linked Polymer Thin Film

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## Experimental Section

### Measurement of reactivity ratios between THPEMA (1) and GMA or styrene (2)

The reactivity ratio studies were performed according to a procedure modified from the literature.[1] A stock solution of AIBN in anisole was prepared by adding 95.5 mg of AIBN in 25 mL of anisole. 5 mL of the stock solution were added into 5 different Schlenk flasks containing varying molar ratios of THPEMA : GMA or styrene. The total amount of monomers was fixed at a [monomer]:[AIBN] = 100:1 and the feed ratio for each solution was measured by $^1$H-NMR analysis. All reaction mixtures were subjected to three cycles of freeze-pump-thaw and back filled with Ar. Polymerizations were then conducted by heating the reaction mixtures at 70 °C for 1.5h. Aliquots of the reaction mixtures were taken at this point and analyzed by $^1$H-NMR. The resulting polymers were then precipitated in methanol, filtered, and dried under vacuum. The final copolymer composition was determined by $^1$H-NMR.

A Fineman-Ross plot[2] was constructed to determine the reactivity ratios between THPEMA (1) and GMA or styrene (2). This plot consists of the following equation,

$$x\left(1-\frac{1}{y}\right)=r_1\left(\frac{x^2}{y}\right)-r_2$$

where $x=\frac{[M_1]}{[M_2]}$ and $y=\frac{d[M_1]}{d[M_2]}$. [$M_x$] and d[$M_x$] were obtained from the $^1$H-NMR analysis of the feed, crude and purified copolymers. The reactivity ratios $r_1$ and $r_2$ are then given by the slope and intercept, respectively. For THPEMA and GMA, $r_{GMA}$ = 1.014 and $r_{THPEMA}$= 0.999 which corresponds to an ideal copolymerization. For THPEMA and GMA, $r_{styrene}$ = 0.738 and $r_{THPEMA}$= 0.587.

## Supplementary Figures

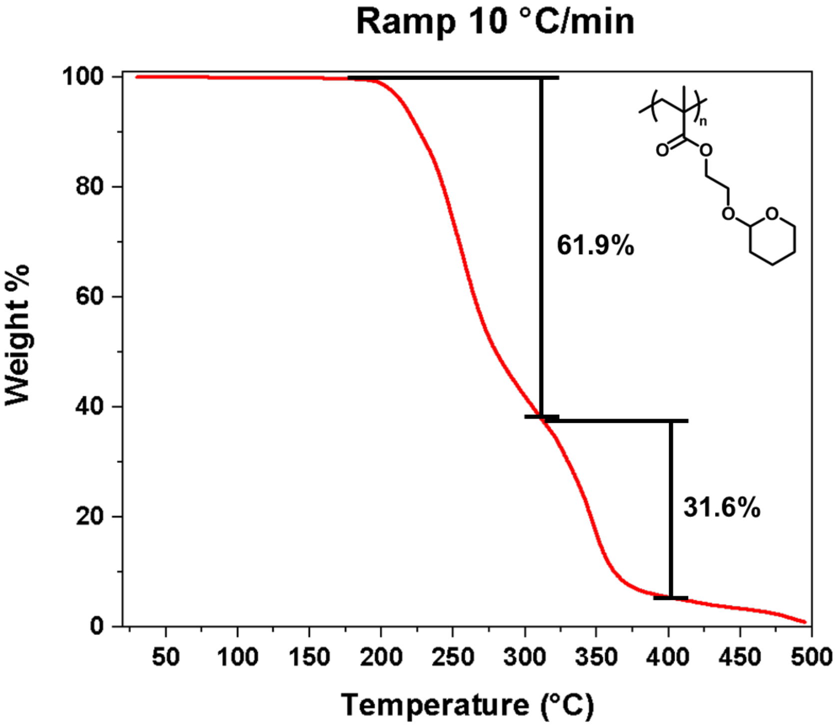


**Figure S1.** Ramp TGA of a THPEMA homopolymer synthesized by ATRP ($\overline{M_n}$ = 71.2kDa, Đ = 1.53) showing a 2-stage decomposition with a decomposition temperature ($T_d$, 5% weight loss temperature) of 215 °C.

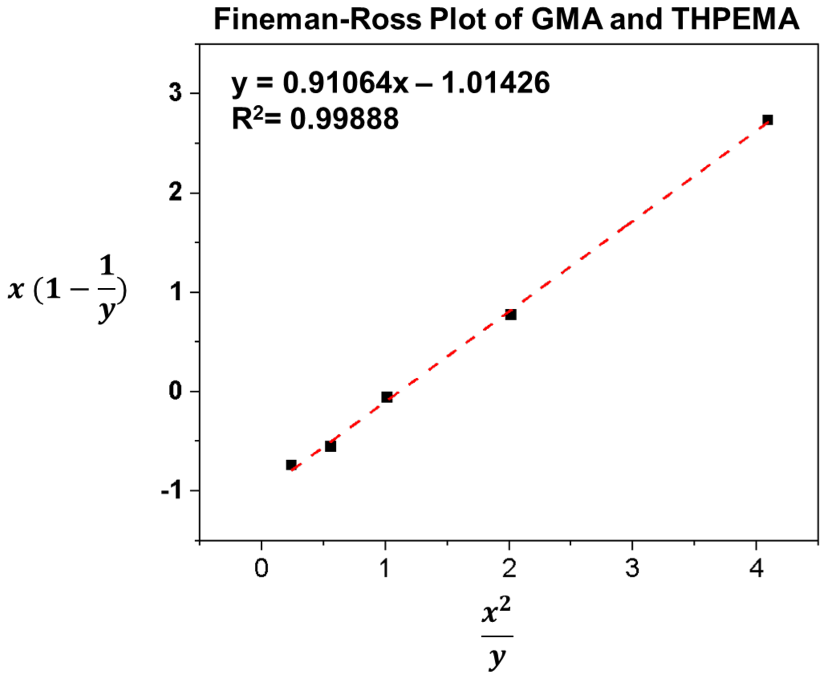


**Figure S2.** Fineman-Ross Plot of the copolymerization of GMA and THPEMA yields $r_{GMA}$ = 1.014 and $r_{THPEMA}$= 0.999.

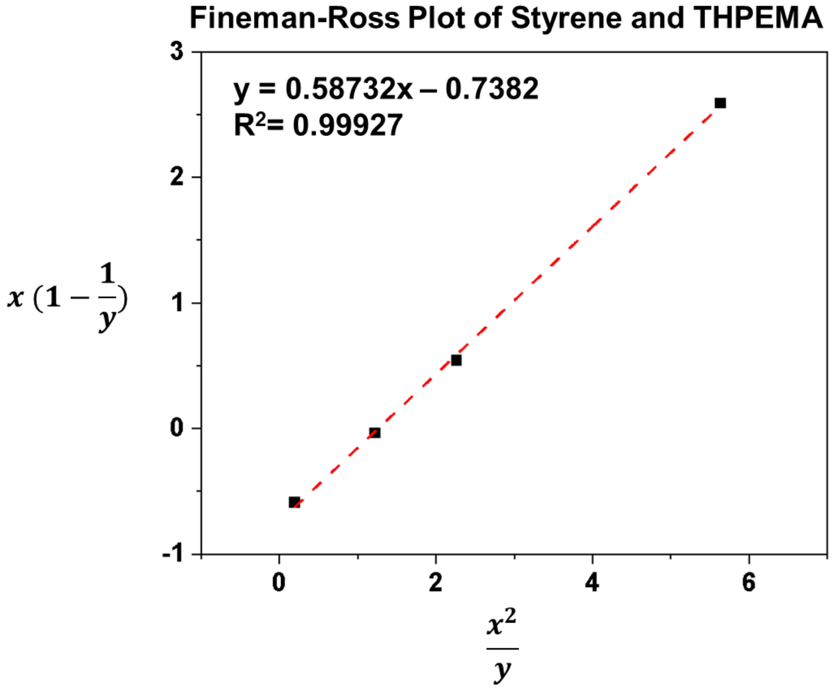


**Figure S3.** Fineman-Ross Plot of the copolymerization of styrene and THPEMA yields $r_{styrene}$ = 0.738 and $r_{THPEMA}$= 0.587.

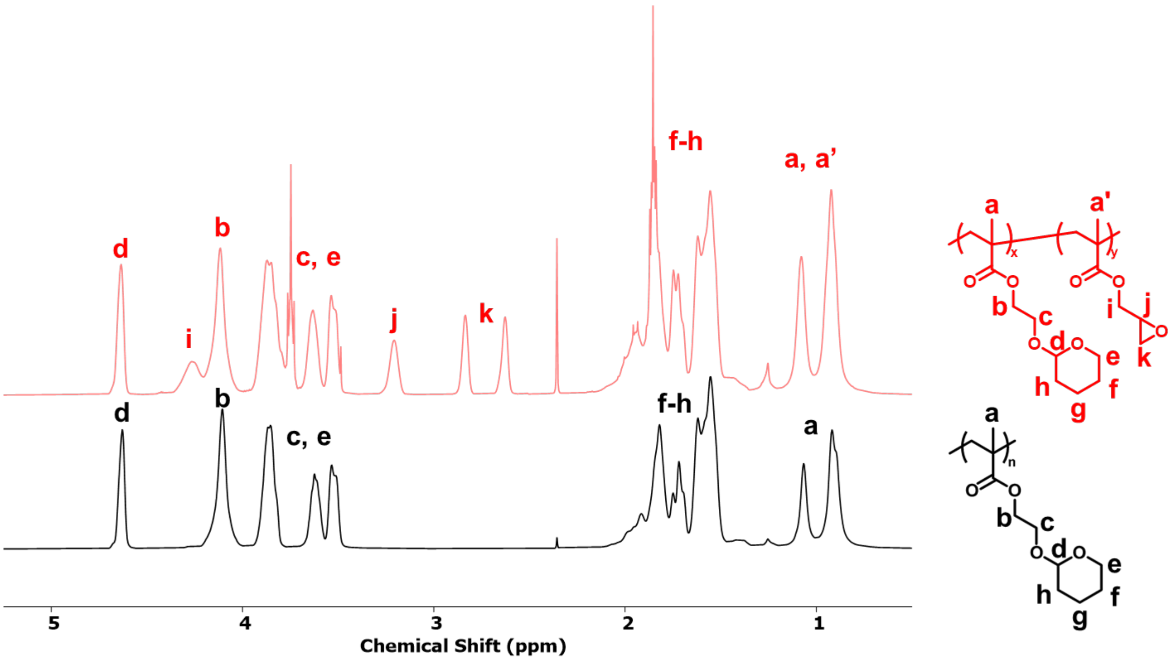


**Figure S4.** $^1$H-NMR of a homopolymer of THPEMA (black) and a random copolymer GMA and THPEMA (red).

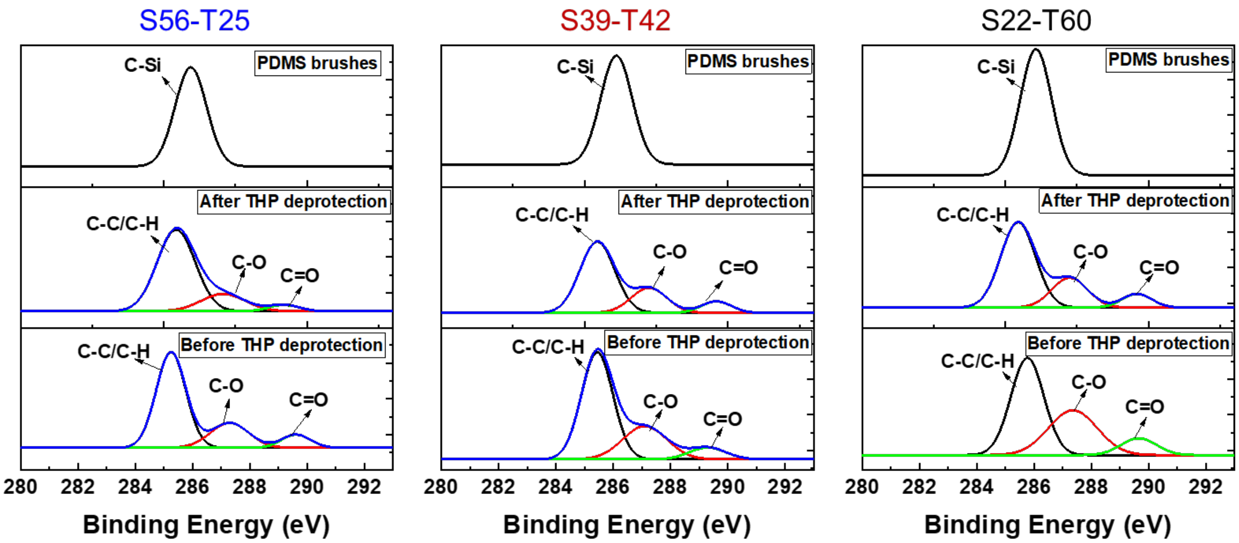


**Figure S5.** Deconvoluted high resolution C1s XPS spectra of the inimer coating before and after THP group deprotection and PDMS brush growth.

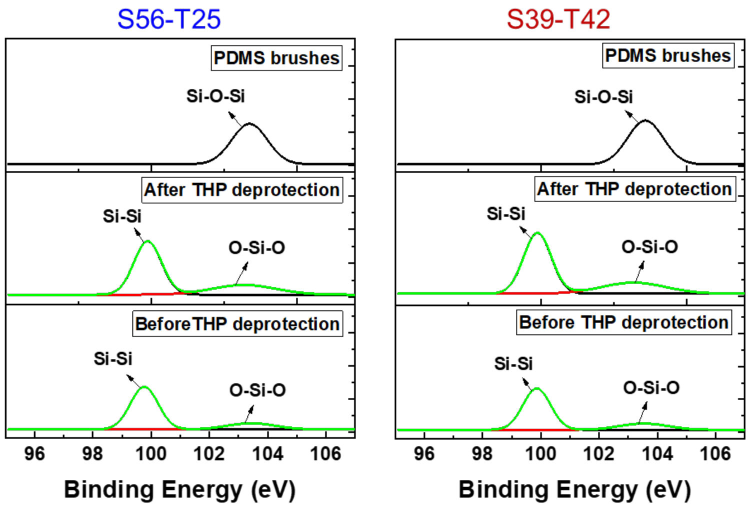
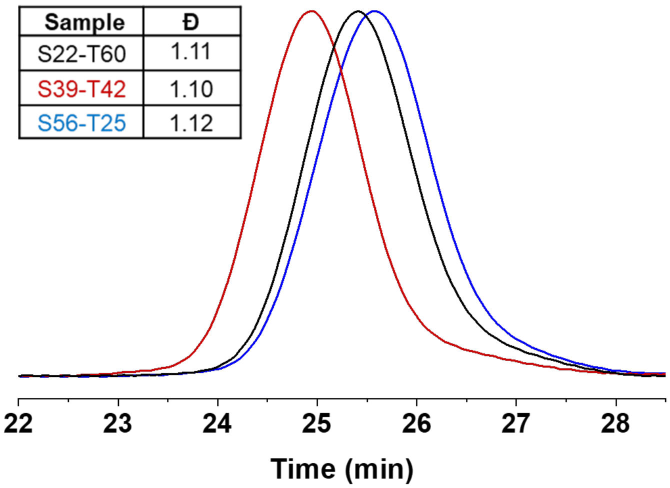


**Figure S6.** Deconvoluted high resolution Si2p XPS spectra of the inimer coating before and after THP group deprotection and PDMS brush growth.



| Sample | Đ |
|---|---|
| S22-T60 | 1.11 |
| S39-T42 | 1.10 |
| S56-T25 | 1.12 |

**Figure S7.** SEC traces of PDMS grown in solution during PDMS brush growth.

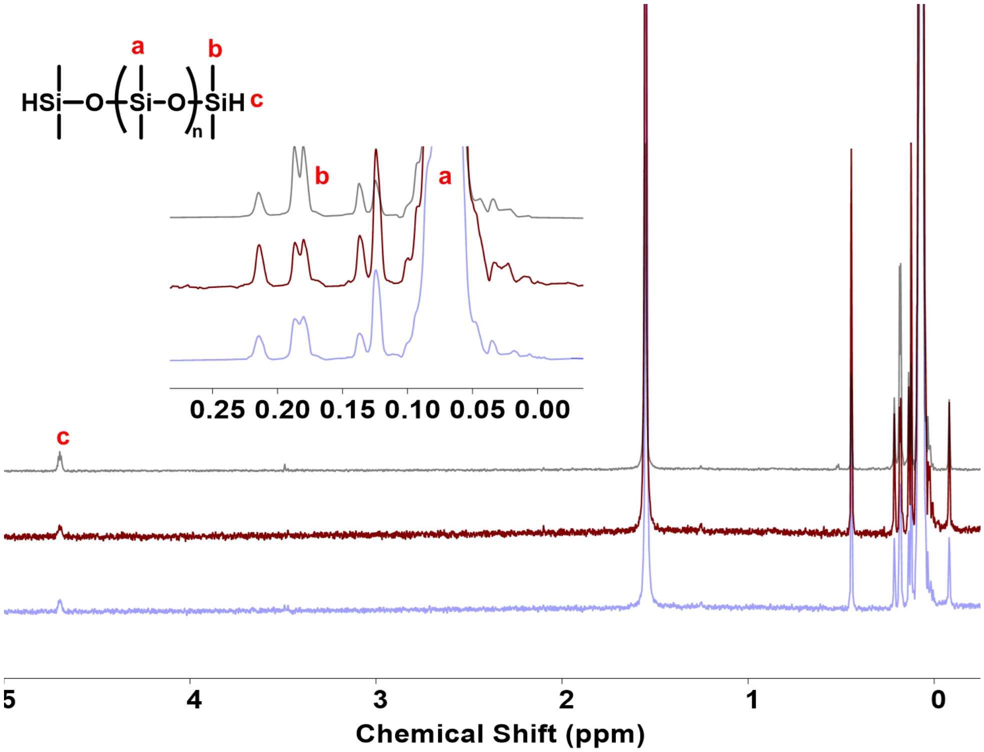


**Figure S8.** $^1$H-NMR spectra of PDMS grown in solution during PDMS brush growth for S56-T25 (blue), S39-T42 (maroon), and S22-T60 (black).

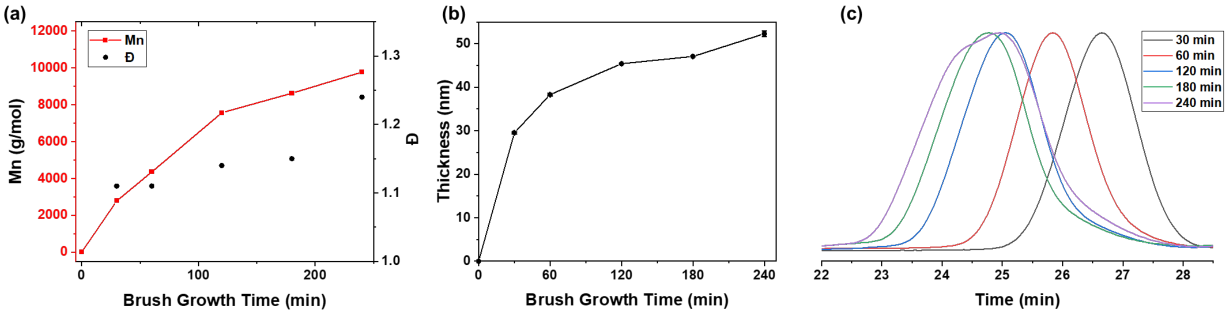
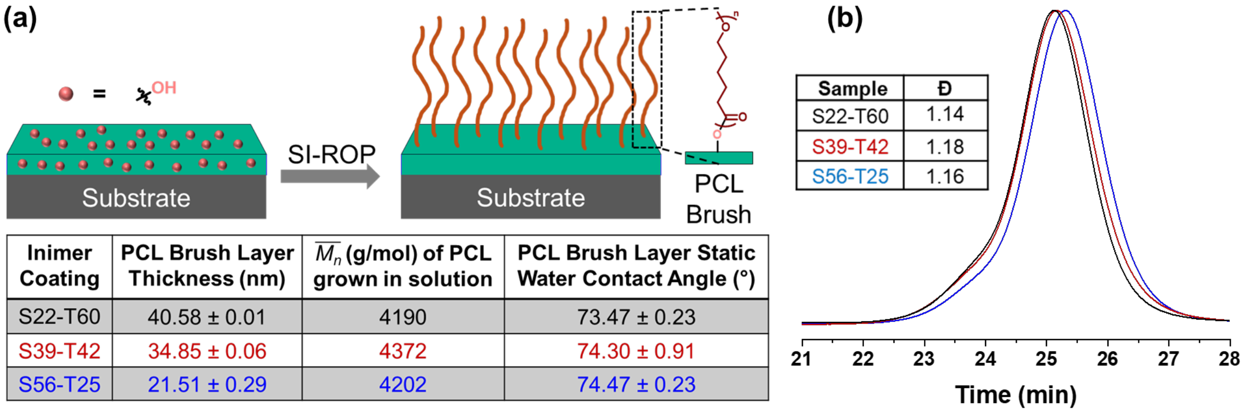


**Figure S9.** Plots showing the a) $M_n$ and Đ of the PDMS grown in solution as a function of polymerization time during organocatalytic SI-ATRP of $D_3$ and b) the linear increase in brush thickness as a function of time. c) SEC traces of the PDMS grown in solution.



| Inimer Coating | PCL Brush Layer Thickness (nm) | $\overline{M_n}$ (g/mol) of PCL grown in solution | PCL Brush Layer Static Water Contact Angle (°) |
|---|---|---|---|
| S22-T60 | 40.58 ± 0.01 | 4190 | 73.47 ± 0.23 |
| S39-T42 | 34.85 ± 0.06 | 4372 | 74.30 ± 0.91 |
| S56-T25 | 21.51 ± 0.29 | 4202 | 74.47 ± 0.23 |

| Sample | Đ |
|---|---|
| S22-T60 | 1.14 |
| S39-T42 | 1.18 |
| S56-T25 | 1.16 |

**Figure S10.** a) Schematic representation of PCL brush growth by organocatalytic SI-ROP. The PCL brush layer thickness, static water contact angle, and $\overline{M_n}$ of the PCL grown in solution for all inimer coatings is presented. The $\overline{M_n}$ was calculated by $^1$H-NMR end group analysis. b) SEC traces of the PCL grown in solution for all inimer coatings.

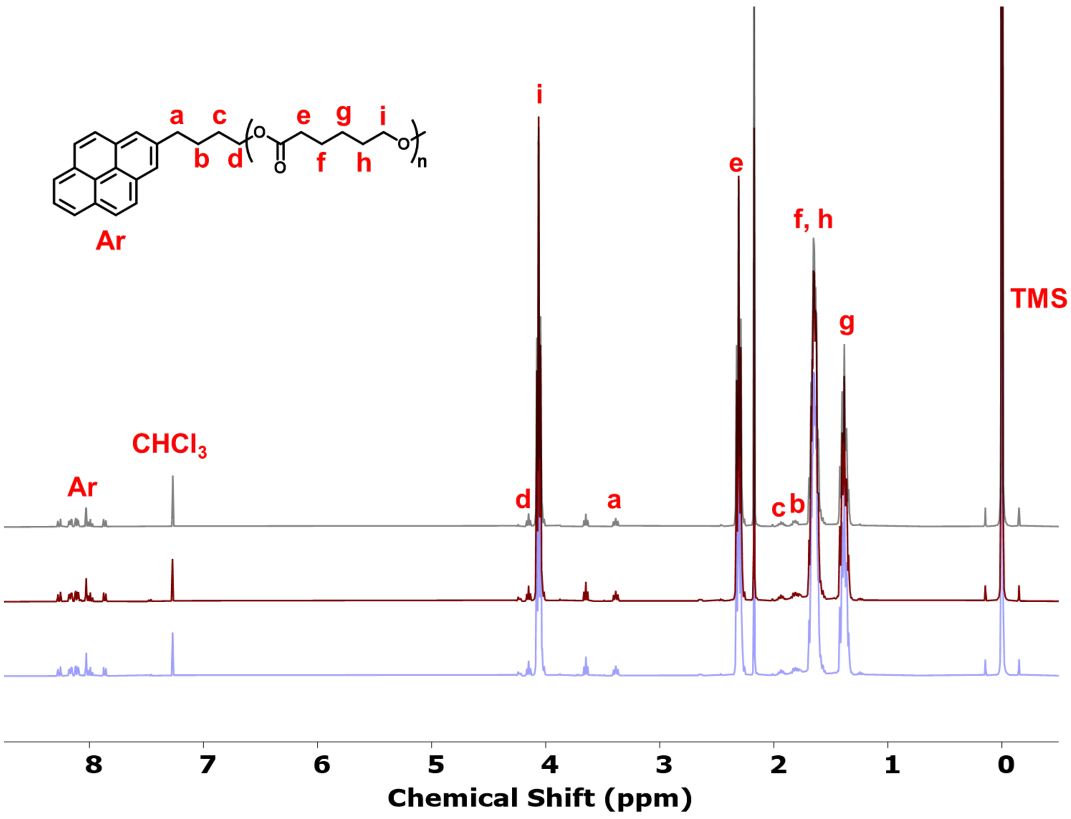


**Figure S11.** $^1$H-NMR spectra of PCL grown in solution during PCL brush growth for S56-T25 (blue), S39-T42 (maroon), and S22-T60 (black).

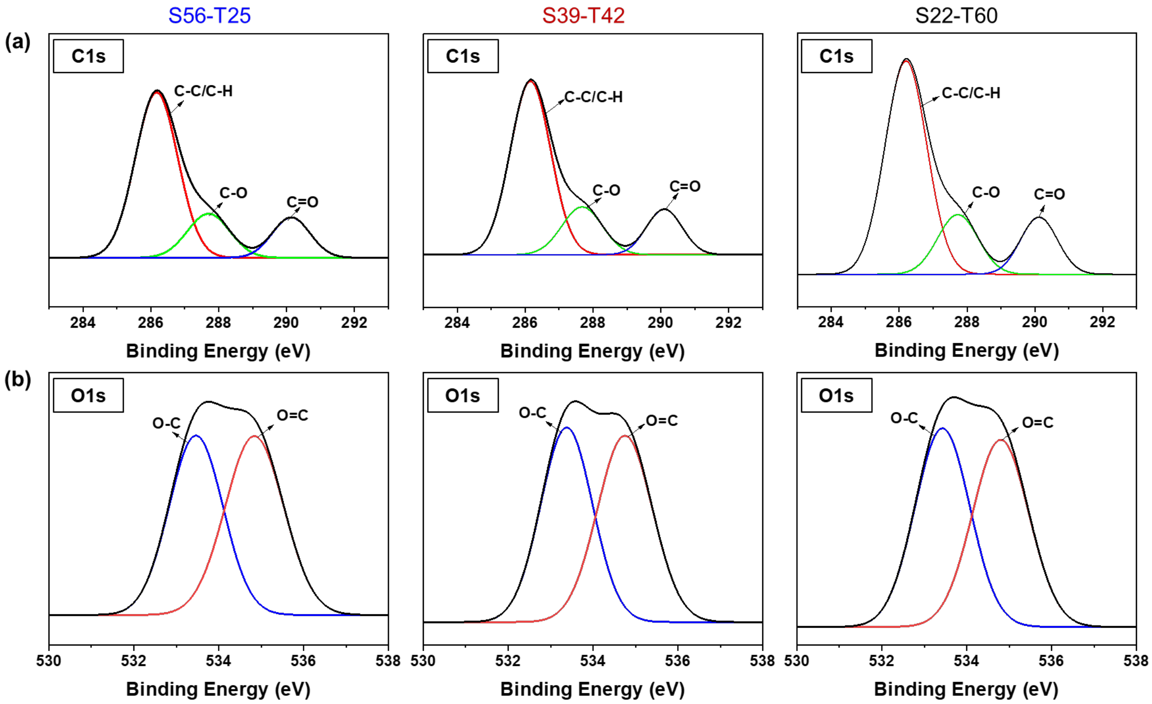


**Figure S12.** Deconvoluted high resolution a) C1s and b) O1s XPS spectra of PCL brushes grown from the different inimer coatings.

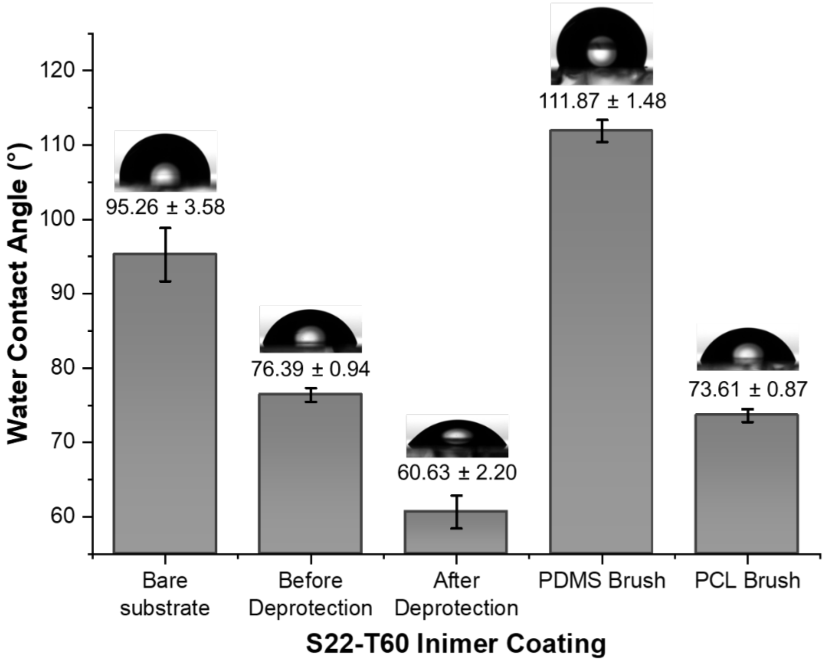


**Figure S13.** Static water contact angle measurements for PDMS and PCL brushes with thickness of 35.53 ± 1.46 nm and 36.86 ± 2.71 nm, respectively, grown from a S22-T60 inimer coating on a gold substrate.

**Table S1.** Thickness and water static contact angle measurements of a S22-T60 inimer coating before and after sonicating in toluene for 20 minutes.

| **Inimer Coating** | **Before Sonication** | | **After Sonication** | |
|---|---|---|---|---|
| | **Thickness (nm)** | **Contact Angle (°)** | **Thickness (nm)** | **Contact Angle (°)** |
| S22-T60 | 4.48 ± 0.04 | 80.22 ± 0.87 | 3.87 ± 0.14 | 78.31 ± 0.51 |

**Table S2.** Thickness of the inimer coatings after deprotection.

| **Inimer Coating** | **Thickness (nm)** |
|---|---|
| S22-T60 | 3.79 ± 0.03 |
| S39-T42 | 4.34 ± 0.19 |
| S56-T25 | 3.95 ± 0.03 |

**Table S3.** Integrated area  of C1s and deconvoluted C-O peak for three inimer coatings.

| | **S56-T25** | | **S39-T42** | | **S22-T60** | |
|---|---|---|---|---|---|---|
| | **Before deprotection** | **After deprotection** | **Before deprotection** | **After deprotection** | **Before deprotection** | **After deprotection** |
| $\mathbf{A_{C1s}}$ | 1.475 | 1.094 | 1.680 | 1.287 | 1.915 | 1.465 |
| $\mathbf{A_{C\text{-}O}}$ | 0.3376 | 0.1717 | 0.4664 | 0.2947 | 0.6972 | 0.3535 |
| $\mathbf{A_{C1s} / A_{C\text{-}O}}$ | 0.2228 | 0.156 | 0.2776 | 0.2289 | 0.3640 | 0.241 |

**Table S4.** Contour length of the PDMS grown from free initiator in brush growth solution compared to the brush layer thickness.

| **Inimer Coating** | **DP of PDMS grown from free initiator**[a] | **Contour Length**[b] **(nm)** | **Brush Layer Thickness (nm)** |
|---|---|---|---|
| S22-T60 | 76.1 | 12.48 | 36.21 ± 0.03 |
| S39-T42 | 102.3 | 16.78 | 33.64 ± 0.33 |
| S56-T25 | 80.1 | 13.4 | 17.31 ± 0.17 |

[a] Calculated using $^1$H-NMR

[b] Calculated using the PDMS repeat unit length reported in the literature.[3] Contour length = DP x 0.164nm.

**Table S5.** Contour length of the PCL grown from free initiator in brush growth solution compared to the brush layer thickness.

| **Inimer Coating** | **DP of PCL grown from free initiator**[a] | **Contour Length**[b] **(nm)** | **Brush Layer Thickness (nm)** |
|---|---|---|---|
| S22-T60 | 36.7 | 27.5 | 40.58 ± 0.01 |
| S39-T42 | 38.3 | 28.7 | 34.85 ± 0.06 |
| S56-T25 | 36.8 | 27.6 | 21.51 ± 0.29 |

[a] Calculated using $^1$H-NMR

[b] Contour length = DP x 0.75nm. PCL repeat unit length was calculated using computational methods.[4]

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