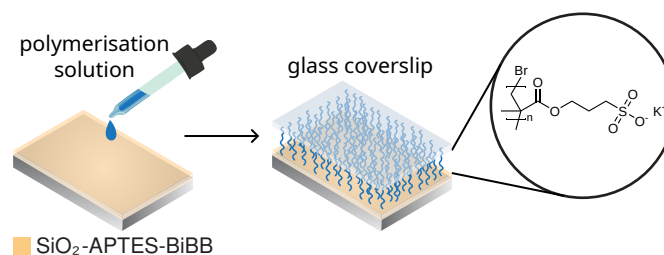# Scalable air-tolerant µL-volume synthesis of thick poly(SPMA) brushes using SI-ARGET-ATRP

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**Abstract**

We present a straightforward procedure for preparing thick (up to 300 nm) poly(3-sulfopropyl methacrylate) brushes using SI-ARGET-ATRP by conducting the reaction in a fluid film between the substrate and a coverslip. This method is advantageous in a number of ways: it does not require deoxygenation of the reaction solution, and the monomer conversion is much higher than usual since only a minimal amount of solution (microliters) is used, resulting in a tremendous reduction (~50x) of wasted reagents. Moreover, this method is particularly suited for grafting brushes to large substrates.

## 1 Introduction

Polymer brushes are coatings consisting of macromolecules end-grafted to a surface at densities sufficiently high that the chains are forced to stretch away [1, 2]. They can be used in a broad range of applications, from sensors [3, 4] to lubricants [5, 6] and antifouling surfaces [7, 8], in liquid and in air [9]. There are two general ways of creating polymer brushes: *grafting-from* [10], in which polymers are grown from an initiator-functionalized surface, and *grafting-to* [11, 12, 13], in which pre-synthesized polymers are immobilized on a surface. Grafting-to is generally easier to perform, and allows better control over the chain length (distribution), but suffers from a drawback: attainable grafting densities are typically low as steric hindrance of already grafted chains precludes the grafting of additional chains.

Polymer brushes can be prepared in a grafting-from manner using surface-initiated polymerizations such as atom-transfer radical polymerization (SI-ATRP) [14, 15]. However, conventional ATRP has a couple of drawbacks, most notably the fact that it is oxygen-sensitive and thus has to be carried out under anaerobic conditions. This complicates synthesis of polymer brushes using ATRP significantly in a few ways. Most import-antly, it requires the use of airtight reaction vessels and rigorous deoxygenation of reaction solutions (e.g. by purging with an inert gas like nitrogen). Even small amounts of oxygen inadvertently introduced into the system (e.g. by inadequate deoxygenation of a reactant, or an air leak) will result into termination of the polymerization reaction. Moreover, it means scaling up to larger surfaces is difficult, since equally large air-tight glassware (to contain them) is required, and conversion is extremely low; only a small fraction of monomer in the solution is polymerized on the surface. [16, 17]

Air-tolerant polymerization methods greatly simplify polymer brush synthesis [18, 19, 20], and make it accessible to more people, as well as much more convenient for experienced chemists. Air-tolerant ATRP methods, most of which are based on activator regeneration, have been developed (initially for solution ATRP, and later adapted to surface-initiated ATRP) by the Matyjaszewski group [16, 17, 21].

ATRP is a reversible-deactivation radical polymerization (RDRP, also called controlled radical polymerization) system in which the equilibrium between propagating and dormant chain ends is mediated by transfer of a halide to a transition metal catalyst (usually copper) [15, 22]. The mechanism by which oxygen interferes with ATRP is by oxidising the Cu(I)-

ligand complex (the activator species) to Cu(II), as well as by quenching the propagating radicals, although the former mechanism dominates over the latter at ATRP equilibrium because of the low concentration of propagating chain ends. Activator regeneration methods are based on continuously *regenerating* the activator species by steadily reducing Cu(II) back to Cu(I). In activators regenerated by electron transfer (ARGET), this is achieved using an excess of a slowly-reacting non-radical forming reducing agent. In this way, the system formed by the Cu catalyst and reducing agent act as a kind of oxygen scavenger. The same mechanism also allows for a tremendous reduction of catalyst concentrations, to (sub-)100 ppm levels (relative to monomer): although in principle only the *ratio* of Cu(I) to Cu(II) affects the polymerization kinetics, in reality with normal ATRP a rather large absolute quantity of catalyst is required as a buffer, since inevitable chain termination reactions irreversibly convert Cu(I) to Cu(II). With ARGET, the accumulated Cu(II) is continuously reduced back to Cu(I). [16, 22, 23]

Note that activator regeneration methods only render ATRP oxygen tolerant to a limited extent, since the rate of oxygen diffusion into the system should not exceed the activator regeneration rate. This unfortunately means conducting ATRP wholly open to air is still not feasible, since in that case the rate of oxygen diffusion typically exceeds the activator regeneration rate. However, these methods do enable conducting ATRP without the need to deoxygenate the solution, as long as measures are taken to limit fresh air exchange during the polymerization, for example by using sealed vessels like capped vials or jars. [16]

Instead of using milliliters of solution in sealed vessels, the reaction volume can be reduced by conducting the reaction in a fluid film between the substrate and a coverslip employed as an oxygen barrier [24]. This significantly reduces the amount of wasted monomer and other reagents, and facilitates scalability. Recently, Flejszar et. al. reported a procedure for polymerising 2-(dimethylamino)ethyl methacrylate (DMAEMA) using SI-ARGET-ATRP under a coverslip to limit oxygen exposure [25]. DMAEMA is special as a monomer for ARGET-ATRP because it itself acts as a reducing agent [26], eliminating the need for a dedicated one.

In contrast to the work of Flejszar, we have to use a dedicated reducing agent because SPMA does not have intrinsic reducing properties like DMAEMA does. In this article, we present the process and results of adapting and optimising Flejszar et. al.'s method of SI-ARGET-ATRP under a coverslip to 3-sulfopropyl methacrylate (SPMA), a anionic monomer that yields strongly hydrophilic polyelectrolyte brushes. The Design of Experiments (DoE) principle is employed to systematically vary various parameters, with the goal of determining their effects, and ultimately, finding the optimal conditions.

## 2 Materials and methods

### Materials

Potassium 3-sulfopropyl methacrylate (SPMAK, 98%), (3-aminopropyl)triethoxysilane (APTES, 98%), α-bromo-isobutyryl bromide (BiBB, 98%), 2,2'-bipyridine (BiPy, 98%), triethylamine (TEA, 98%), ascorbic acid (AA), copper(II) chloride ($CuCl_2$), toluene (99.5%), and methanol (99.8%) are purchased from Merck and used as received.

Silicon wafers ($\varnothing 10$ cm, $525$ μm thick, boron-doped with (100) crystal lattice orientation) are purchased from Okmetic.

### Preparation of initiator-functionalized silicon substrates

Silicon wafers are cut into pieces, rinsed with water and ethanol, and dried under a nitrogen stream. The substrates are cleaned and activated by plasma cleaning with oxygen plasma for 20 min and subsequently functionalized by vapor deposition of APTES (0.1 mL) in a desiccator under vacuum overnight. Next, they are rinsed and dried again and the initiator (BiBB) is coupled by reaction in a solution consisting of 100 mL of toluene, 1 mL of TEA, and 1 mL of BiBB for 3 h. The reaction mixture is vigorously stirred to prevent settling of aggregates on the substrates. After the reaction, the samples are thoroughly rinsed and dried once again.

### Surface-initiated polymerization of SPMA by ARGET-ATRP

A stock solution ('ATRP cocktail') containing the monomer (SPMAK), copper halide salt (CuCl2), and ligand (BiPy) in 4:1 water to methanol is prepared. The concentrations are systematically varied to determine optimal condictions as described in the results section. Another stock solution of 50 mM ascorbic acid in water is made. The latter solution has to be prepared fresh daily unless stored under anaerobic conditions, since aqueous solutions of ascorbic acid are not stable in aerobic conditions.

The initiator-functionalized substrates are placed on a flat surface and a desired volume (typically 100 μL per substrate of 1 cm$^2$) of 'ATRP cocktail' is mixed with an amount of ascorbic acid stock solution in an Eppendorf tube. An immediate color change from very light blue to light orange confirms the reduction of Cu(II) to Cu(I). After pipette mixing, the drops of the solution are deposited on the substrates and covered with a glass coverslip, taking care not to trap any air bubbles, as these will create local defects in the resulting brush. The substrates are covered with a petridish to minimize air currents and left to polymerize for the desired amount of time. To terminate the polymerization, the
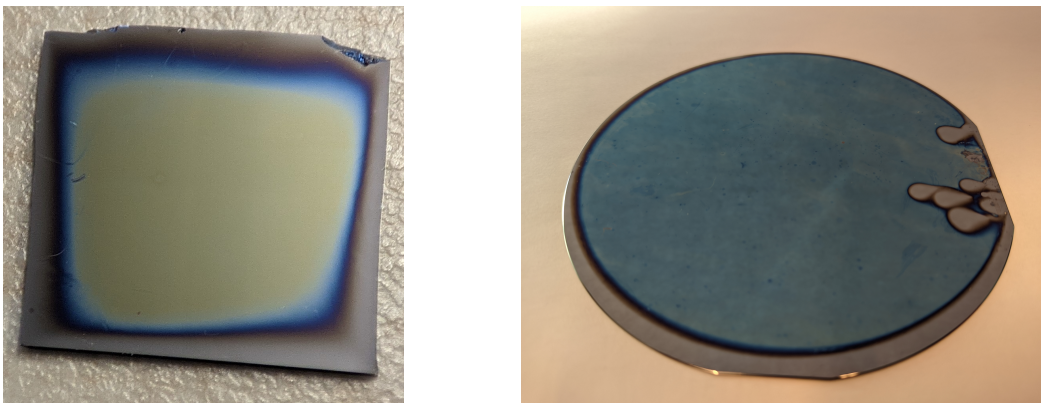
**Figure 1: Left:** *poly(SPMA) brush on a* $1\,cm^2$ *piece of silicon. Note the thickness gradient at the edges, which occurs due to oxygen diffusion.* **Right:** *an entire* $\varnothing 10\,cm$ *silicon wafer grafted with poly(SPMA). The 'holes' are due to entrapment of air bubbles at those positions.*

coverslips are removed and the samples are rinsed with water and ethanol and dried.

## Determination of brush thickness using ellipsometry

The (dry) thickness of brushes is determined using a J.A. Woollam M-2000X variable angle spectroscopic ellipsometer (VASE). Measurements are performed at angles of 65, 70, and 75° and at wavelengths between 300 and 1000 nm.

The ellipsometric data is fitted using the Complete-EASE software to a model composed of a Si substrate, a 1 nm native oxide layer, and a Cauchy layer for the polymer brush. This topmost layer's thickness and Cauchy A and B parameters are fitted. We do not use higher-order Cauchy coefficients, and we assume the film is transparent over the measured wavelength range.

## 3 Results and discussion

Kim et. al. presented a recipe for the surface-initiated polymerization of various monomers including SPMA using ARGET-ATRP (in a closed vial, without deoxygenation) [27], which is used as a starting point (Table 1). Here, a catalyst concentration of 100 ppm is used, and the ligand is present in a 6x excess to the copper. The solvent is a 4:1 mixture of water and methanol. Kim et. al. report around 90 nm thick brushes after 4 h using this recipe.

**Table 1:** *Recipe by Kim et. al. [27]*

| SPMA (mM) | CuBr2 (mM) | BiPy (mM) | Ascorbic acid (mM) |
|---|---|---|---|
| 620 | 0.063 | 0.38 | 3.1 |

We reproduced this recipe (in a closed vial with 3.3 mL solution) with some small changes: $CuCl_2$ instead of $CuBr_2$, and a 10x instead of a 6x excess of ligand. The

former is expected to slightly improve control [28], and a substantial excess of ligand to copper is known to be beneficial in aqueous ARGET-ATRP, because in water the Cu(I)/ligand complex is liable to dissociate. An excess of ligand shifts the equilibrium towards the Cu(I)/ligand species [29]. At 4 h polymerization, we obtain 140 nm thick brushes, and a fairly linear thickness-over-time relationship between 2 and 6 h.

PMDETA instead of BiPy as a ligand was also tried, but this only yielded thin brushes (no thicker than 50 nm after 4 h) and uncontrolled polymerization (non-linear thickness over time). It is not completely clear why the polymerization is so poorly controlled with PMDETA, but it is mentioned in literature that the Cu(II)/PMDETA complex is unstable towards protonation, which could be problematic in ARGET as protons are released as a side product of the oxidation of the reducing agent [22].

Entries 1–3 in Table 2 show the results of a first experiment using this recipe (and a higher and lower reducing agent concentration) performed under a coverslip. This successfully resulted in homogeneous brushes with the exception of a notable thickness gradient of a few mm wide around the edges, caused by oxygen diffusion from the surrounding air (see Figure 1). This 'edge effect' has been noted by others performing air-tolerant SI-ATRP in a liquid film sandwiched between the substrate and a cover [17, 24]. The reducing agent concentration was varied first, as that parameter is expected to be most critical when changing the setup (and thus, the amount of oxygen diffusion). Predicting the optimal amount of reducing agent is not trivial: too much will produce too much activator (Cu(I)) in the beginning of the polymerization reaction, leading to overly fast and poorly controlled ATRP. On the other hand, an insufficient amount of reducing agent results in poor oxygen tolerance, and thereby too slow polymerization (or none at all) [21]. Both cases result in thin brushes. This experiment clearly
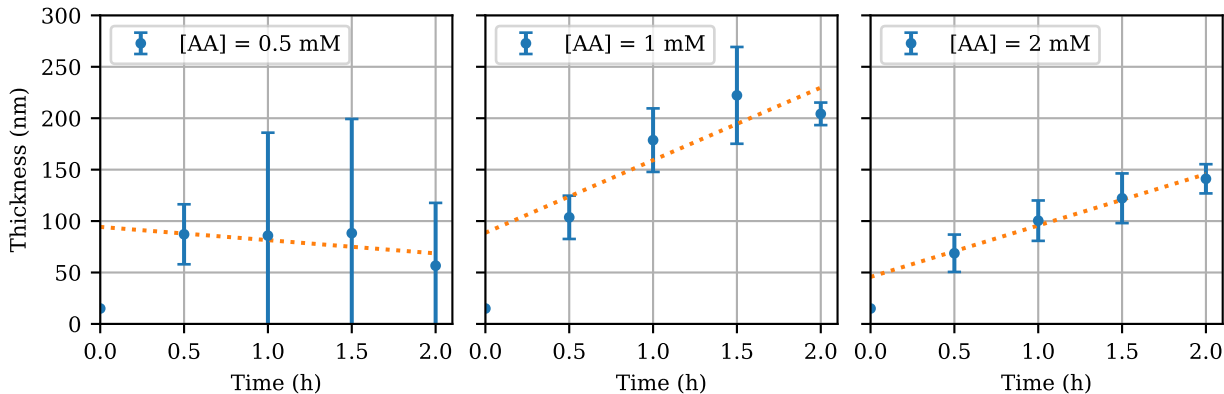
**Figure 2:** *Kinetics for several values of the reducing agent concentration with 90% confidence intervals and linear fits. A linear increase in thickness over time is expected in the case of good polymerization control. For the lowest reducing agent concentration of 0.5 mM, brushes with wildly fluctuating thicknesses are obtained because of insufficient oxygen tolerance.*

shows that 10 mM ascorbic acid is excessive, since it results in thinner brushes than are obtained with lower concentrations.

**Table 2:** *Initially tried recipes for polymerization under a coverslip.*

| # | [M] (mM) | [Cu] (mM) | [RA] (mM) | Thickness (nm) | |
|---|---|---|---|---|---|
| | | | | 2 h | 4 h |
| 1 | 620 | 0.063 | 3.1 | 141.44 | 97.51* |
| 2 | 620 | 0.063 | 1.5 | 115.62 | 123.39 |
| 3 | 620 | 0.063 | 10.0 | 62.47 | 75.67 |
| 4 | 1000 | 0.200 | 2.0 | 219.54 | - |

Next, a full factorial design was performed with three factors (monomer concentration, catalyst concentration, and reducing agent concentration) and two levels, i.e. a $2^3$ design. From this, it was identified that the higher monomer concentration (1 M), higher catalyst concentration (0.2 mM), and lower reducing agent concentration (2 mM) produced the thickest brushes (# 4 in Table 2). The full results are available in the SI.

Reducing the reducing agent concentration further to 1 mM yielded even thicker brushes, indicating that we are still in the regime of 'overly fast ATRP'. However, when the reducing agent concentration was again cut in half to 0.5 mM, brushes with inconsistent thicknesses and large edge gradients were obtained. Likely, 0.5 mM of ascorbic acid does not provide sufficient oxygen tolerance, making the process too susceptible to small variations in oxygen ingress, and thereby yielding inconsistent results. Therefore, ARGET-ATRP in this configuration presents a trade-off between oxygen tolerance and polymerization control; in contrast to ATRP performed under anaerobic conditions, lowering the reducing agent concentration does not per se lead

to better control over thickness. The results of the kinetic study for several reducing agent concentrations are shown in Figure 2.

This method was successfully applied to larger substrates, such as whole 10 cm Si wafers (see Figure 1 right). Instead of covering them with a coverslip, two equally sized substrates can simply be sandwiched together, sharing the liquid film of polymerization solution between them. This further increases the efficiency of the process, as only half the amount of reagent per area polymer brush is required.

Thick (>200 nm) brushes sometimes developed a hazy, rough finish (see SI). It was not possible to remove this haze by rinsing or ultrasonic cleaning without also completely degrafting the brush. However, using a more resilient APTES-PGMA-TRIS grafting layer[1] instead of APTES permitted the removal of the haze without degrafting the brush. Although we were not able to ascertain the exact mechanism behind the emergence of the surface roughness, we postulate that it is caused by non-grafted polymer that entangles with the brush at sufficiently high chain lengths. Moreover, we found that the issue could be prevented by more thoroughly cleaning the wafers after initiator coupling by ultrasonic cleaning for 5 min in an ethanol/water mixture. This suggests that surplus physisorbed BiBB that is present on the wafers when they are not adequately cleaned is the source of non-grafted polymer.

Finally, retention of chain-end functionality was confirmed by a chain extension experiment, in which the same wafer is polymerized in multiple steps, and its thickness is measured in between (Figure 3). This technique can also be used to produce block copolymer

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[1] It is well-known that brushes grafted from silane-based anchors can degraft [30]. The usage of macro-initiators such as poly(glycidyl methacrylate) (PGMA) can significantly improve the resilience against degrafting [31].

brushes.

The successful, homogeneous formation of well-defined poly(SPMA) brushes was confirmed by FTIR spectroscopy, AFM, and optical microscopy (see SI).
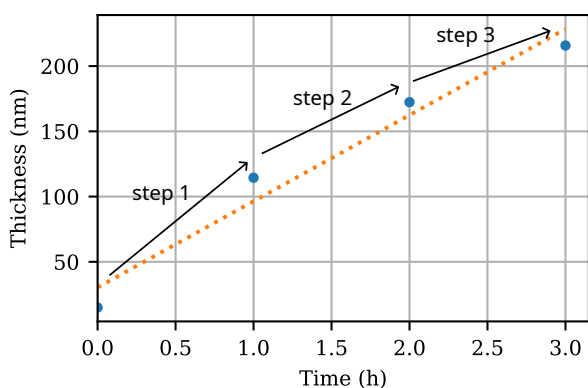


***Figure 3:*** *Thickness of a polymer brush grown in multiple steps (chain extension).*

## 4   Conclusion and outlook

In summary, we presented an air-tolerant SI-ARGET-ATRP synthesis of poly(SPMA) brushes on silicon wafers that does not require any deoxygenation or inert atmosphere by performing the polymerization under a coverslip in order to seal it off from oxygen. This results in a tremendous reduction in (wasted) reagents and required glassware, and facilitates scaling up to large surfaces.

In particular, we investigated the brush growth kinetics as a function of the reducing agent concentration, which showed a non-trivial influence: while the reducing agent concentration controls the polymerization speed in ARGET-ATRP, in this configuration it also counteracts the effects of oxygen. The fastest brush growth was observed with $1\,\mathrm{mM}$ of ascorbic acid, which yielded a growth rate of $70\,\mathrm{nm\,h^{-1}}$ on average. This method was successfully applied to an entire $\varnothing\,10\,\mathrm{cm}$ silicon wafer.

Although the presence of oxygen in the system complicates the ARGET-ATRP, we believe the advantages of this method outweigh the drawbacks considerably.

## Acknowledgements

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