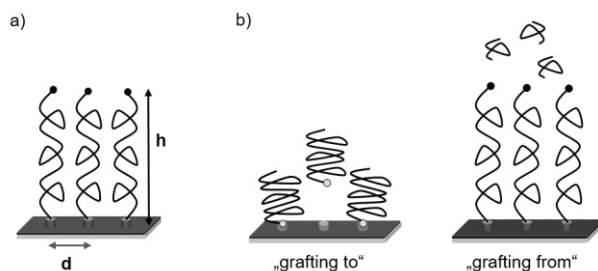


## 2 Introduction to Polymer Brushes

A lot of research has already been carried out focusing on polymer brushes, generated by surface initiated atom transfer radical polymerization (SI-ATRP). Polymer brushes are generally defined as thin layers of polymer chains end-grafted to a surface.<sup>22,23</sup> These polymer chains, which are terminally attached to a surface, have a distance between the chains ( $d$ ), such that  $d$  is less than twice the radius of gyration ( $R_g$ ) of the polymer. Due to chain crowding, the surface tethered macromolecules stretch away from the surface and they are in an entropic equilibrium when they exhibit an extended conformation. This conformation is defined as the equilibrium layer thickness ( $h$ ), as demonstrated in Figure 2.1.<sup>7–9</sup>



**Figure 2.1:** Schematic representation of a) polymer brushes and b) the “grafting to” and “grafting from” approach

Polymer brush layers are typically prepared through covalent attachment, which can be achieved through two available different experimental approaches, namely “grafting to” or “grafting from”-techniques, as shown in Figure 2.1. Both approaches have their unique characteristics.<sup>24,25</sup>

The “grafting to” approach implies the attachment of preformed polymer chains to a surface.<sup>24</sup> The end-functionalized polymer is reacted with reactive sites on a solid surface to form an anchored polymer layer. Once some preformed polymer chains are tethered to the surface, new polymer molecules have to diffuse through the existing attached polymer layer to reach surface active groups. The steric hindrance for surface attachment increases as the thickness of the polymer film increases. This technique is restricted due to the diffusion limited adsorption and steric hindrance of preformed polymers. As a result, low grafting densities are observed, because thick and dense polymer layers are difficult to achieve.<sup>25,26,19</sup> In contrast to the “grafting to” technique, the “grafting from” approach is known to be more suited to produce high grafting densities of chains and thicker films.<sup>6</sup> Due

to the immobilization of initiating groups on the surface, the grafting density of chains is markedly increased. The polymer chains are grown *in situ* from a surface with a high density of initiating species and remain tethered to the substrate.<sup>26,19,27</sup> Because of these attractive properties, the “grafting from” approach has become the preferred option for the synthesis of polymer brushes with high grafting densities, whereas the surface immobilized initiator layer and subsequent *in situ* polymerization is referred to as surface initiated polymerization (SIP).<sup>24</sup>

## 2.1 Surface Initiated Polymerization (SIP)

In recent years, numerous experimental strategies have been developed for the preparation of polymer brushes by surface initiated polymerizations, such as photoiniferter-mediated photopolymerization (PMP), atom transfer radical polymerization (ATRP) and reversible addition-fragmentation transfer (RAFT) polymerization. These polymerization methods allow the synthesis of a wide variety of macromolecules with monomers that cannot be polymerized with the traditional cationic and anionic living polymerization.<sup>23,28,29</sup>

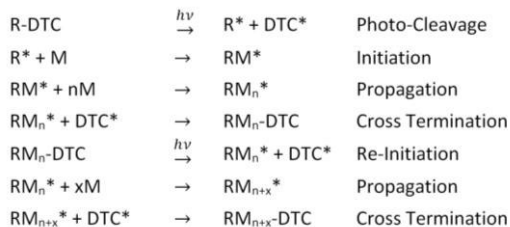
The covalent attachment of polymer chains to solid substrates by SIP is an effective method for the preparation of thick and stable polymer films with tailored surface properties.<sup>29,30</sup> And as the name SIP already implies, does the preparation usually consist of a two-step process the immobilization of an auto-associating group on the substrate surface and the controlled polymerization. The auto-associating molecule is modified with an initiator group.<sup>2,26,31</sup>

### 2.1.1 Photoiniferter-mediated Polymerization (PMP)

The photoiniferter-mediated polymerization explored by Otsu et al. in the early 1980s, is based on the formation of a reactive radical and a relatively stable counter radical, the iniferter (**i**nitiator-**t**ransfer-**t**erminator agent).<sup>32</sup> The iniferter molecule includes a diethyldithiocarbamate functionality, which contains a bond, that cleaves upon exposure to light. One of the radicals resulting from the cleavage, the diethyldithiocarbamyl (DTC) radical, doesn't participate in the initiation, but reacts as a transfer agent and terminating species.<sup>1</sup>

In addition to the less reactive DTC moiety, the photoiniferter dissociates also into a highly reactive carbon radical, which acts as a controlled radical initiator without the addition of any other initiating species. Under correct conditions the DTC radical will cross-terminate with propagating macroradicals (initiated from the carbon radical). And the DTC groups are re-formed as the terminal groups on the polymer chain. Upon further exposure to light, the terminal iniferter species will cleave again and the re-initiation allows more monomer units to insert into the growing chain before another cross-termination occurs.<sup>11</sup> Usually UV labile C-C or

C-S bonds are used as DTC derivatives.<sup>33,34</sup> Figure 2.2 shows a brief, idealized description of the overall mechanism of a photoiniferter-mediated polymerization.



**Figure 2.2: Mechanism of the photoiniferter-mediated polymerization (PMP)**

Propagation occurs by addition of monomers or double bonds to the active centers. The iniferter polymerization mechanism involves two termination pathways: first, the carbon-carbon radical combination and second, the carbon-DTC radical termination. When the viscosity of the polymerizing system is lower and thus, diffusion resistance to termination is low, path one is the significant termination mechanism.<sup>1,13</sup> If the photoiniferter molecules are chemically bound to a surface of a substrate, a polymer chain can be generated in the presence of monomer and during exposure to light. This enables the synthesis of thick polymer brush layers in a relatively short reaction time. Furthermore, the ability to reinitiate the polymerization promotes highly controlled thickness and chemistry of the grafted layer.<sup>16</sup>

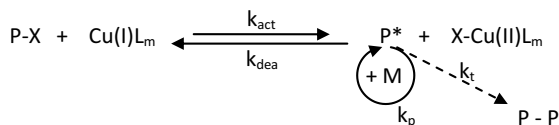
Advantages of this polymerization technique include the facile control of the polymerization reaction by means of irradiation time and UV intensity, which leads to a linear increase of molecular weight (steady growth) with comparatively fast reaction kinetics compared to other methods. This method is compatible with a wide variety of monomers (acrylates, styrenes, acrylonitril and derivatives) and opens the possibility to form block copolymers by reinitiating the polymerization in a different monomer solution.<sup>11</sup> The reaction can be easily performed at room temperature or below, to avoid thermal polymerization and in aqueous media. Additionally, no sacrificial initiator in the monomer solution (limits the formation of free polymers in the bulk solution) required. The technique allows a precise control of the polymer molecular weight and usually yields to polymer brushes with low polydispersity.

### 2.1.2 Atom Transfer Radical Polymerization (ATRP)

In recent years, much attention has been paid to the use of surface initiated atom transfer radical polymerization.<sup>23,28,31,35,36</sup> Because of the ease of initiator formation

and relatively mild polymerization conditions (at ambient temperature in aqueous media), it has been a powerful synthetic strategy to grow polymer brushes from various surfaces, such as gold.<sup>37</sup> In comparison to other controlled radical polymerization techniques, this polymerization is chemically extremely versatile and robust.<sup>38</sup>

ATRP is an effective and convenient method, which tolerates the use of many functional groups, and is easy to apply and results in highly uniform, dense polymer brushes with controlled thickness and composition on surfaces.<sup>6,39-41</sup> The thickness of the film can be adjusted by simply varying the polymerization conditions (i.e., time, monomer concentration, temperature).<sup>35</sup> The main principle of the ATRP reaction is a reversible redox activation of a dormant alkyl halide-terminated polymer chain end by a halogen transfer to a transition metal complex.<sup>36</sup>



**Figure 2.3: Mechanism of the atom transfer radical polymerization (ATRP)**

The formal homolytic cleavage of the carbon-halogen bond, which results from this process, generates a free and active carbon-centered radical species at the polymer chain end. This activation step is based on a single electron transfer of the transition metal complex to the halogen atom, which leads to the oxidation of the transition metal complex. Then in a fast-reversible reaction the oxidized form of the catalyst reconverts the propagating radical chain end to the corresponding halogen capped dormant species.<sup>36</sup> In a typical ATRP reaction, CuCl or CuBr is generally used as a catalyst and bipyridines or multidentate amines as a ligand (L). The ligand must have a high complexation constant to compete with the polyacrylamide for copper, and it must allow fast redox between Cu(I) and Cu(II). Two mechanisms are possible for termination, first a radical transfer can occur from the intended surface bound radical to an AAm monomer in solution and second the Cu(II) species in the solution can act as the catalyst for the extraction of HX in the atom-transfer living polymerization.<sup>42,43</sup>

Significant effort has gone into achieving controlled SI-ATRP. In general, this can be achieved either by adding sacrificial initiator or by adding a Cu(II) salt as a deactivator. In the former case of the sacrificial initiator, a persistent radical is created artificially, because the active amount of conversion and living chains on the surface is too small to establish the standard equilibrium present in bulk ATRP. The disadvantage is the formation of bulk polymers that are difficult to remove.<sup>44</sup> The

addition of Cu(II) can be a good alternative, but adding very small amounts of both Cu(I) and Cu(II) salts in a precise ratio is difficult, because of the oxygen sensitivity of Cu(I). The quenching of the polymerization with Cu(II) species helps to preserve initiation points.<sup>39</sup>

Already a lot of research has been carried out focusing on polymer brushes generated by SI-ATRP. There is no universal recipe and many factors, including the choice of solvents, ligands, monomers and reaction temperature, will affect the polymerization.<sup>45</sup> These parameters can influence the performance of the polymerization, but also offer in the same time a wide range of possibilities to fine tune the reaction.<sup>5</sup> Overall requires the synthesis of polymer brushes by SI-ATRP self-assembled monolayers (SAMs) composed of an active species (the initiator) to graft polymer brushes from a surface.

## 2.2 Self-Assembled Monolayer (SAM)

A SAM is defined as a monomolecular film of a surfactant formed spontaneously on a substrate upon exposure to a surfactant solution.<sup>46</sup> These organic assemblies are formed by the adsorption of molecular constituents having a chemical functionality or headgroup, with special affinity for a substrate.<sup>47</sup> The main chain, also called tail, forms a highly ordered structure oriented away from the substrate, organized by van der Waals interaction and a terminal group, which determines the surface chemistry.<sup>48,49</sup> The main driving forces of the formation of these films are the specific interactions between the reactive head group and the surface of the substrate. Based on these interactions, the SAMs are stable films with a remarkable robustness.<sup>46</sup>

The most molecular monolayers are thiol based adsorbates on gold, which are employed in order to synthesize functional surfaces, to serve as initiator for polymerizations, focusing on covalently attaching a monolayer with high grafting densities on the surface.<sup>10</sup> On surfaces such as glasses, silicon wafers, quartz and mica, an alkoxy silane group is converted into a stable poly(siloxane) layer by coupling with the free hydroxyl group.<sup>2,49</sup> But SAMs have still several limitations. Due to the self-assembling nature of their formation, it is practically impossible to obtain large-area defect-free monolayers. And the monolayers, which are mechanically and chemically fragile, are only several nm thick. In the other case, SAMs can be used to introduce almost any functional group to the surface. Therefore, initiator terminated SAMs provide a conceptionally simple route to grow polymer brushes as robust, functional and switchable surfaces.<sup>50</sup>

The surface wettability, roughness and chemistry are important parameter, which mainly depend on the introduced chemical functionality of the tails of the thiol molecule. As a result, SAMs provide a simple and convenient way to change

surface parameters by altering the terminal groups.<sup>50</sup> If a sample is exposed to a solution containing two different kinds of thiols, a co-adsorption will take place and a binary or mixed monolayer (mixed SAM) will be formed.<sup>51</sup> Generally, the composition of the surface of these mixed SAMs after self-assembly is not identical with the one in the binary solution.<sup>52</sup> In this case, the mixed SAMs could have a non-ideal behavior between the surface and solution compositions.<sup>20,53,54</sup> Another way to introduce two different kinds of thiols onto a gold surface, can be achieved by micro-contact printing ( $\mu$ -CP).

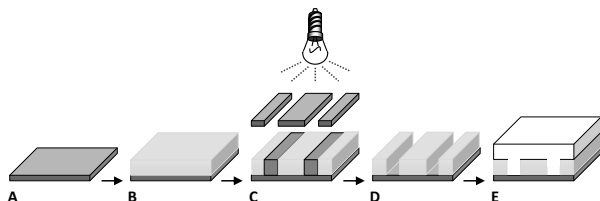
### 2.3 SAMs by Micro-Contact Printing ( $\mu$ -CP)

In recent years, the fabrication of patterned materials on surfaces at ever smaller length scales became more and more interesting, when electrical circuit designs rapidly increased in size and complexity.<sup>55</sup> Photolithography, which is a technology used to generate the initial patterns in electronic circuits, has been extended to pattern other materials. This technology can also be applied to generate patterns of different surface chemistries and is used to control the spatial distribution of other materials. In particular,  $\mu$ -contact printing is a technique with rapid preparation of substrates as well as patterning of a wide range of materials.<sup>56</sup>

$\mu$ -Contact printing is a flexible new technique that forms patterned SAMs with regions terminated with different chemical functionalities, and thus different chemical and physical properties, in patterns with  $\mu\text{m}$  dimensions.<sup>55,57</sup> It has proven to be a useful technique and particularly valuable in the patterning of biological materials.<sup>55</sup> In this method, first described by Whitesides group in 1993, an elastomeric “stamp” is used to transfer an alkanethiol “ink” onto a variety of substrates, for example gold, silver and silicon dioxide, by conformal contact between the stamp and the surface.<sup>58,59</sup> Patterns of binary SAMs, patterned SAMs terminated with one chemical functionality and a background of another, are formed by contact printing one type of molecule and backfilling with another.<sup>59</sup>

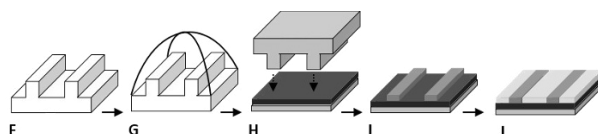
As already mentioned, photolithography is a versatile and precise technique, that routinely generates submicron features. Thereupon, the surface of a silicon wafer (A in Figure 2.4) is coated with a thin and uniform layer of a photoresist, an organic polymer which is sensitive to ultraviolet light (B in Figure 2.4). Then the photoresist is exposed to light through a metal photomask (C in Figure 2.4). The light passes through the mask, generating an area-selective polymerization (degradation) of the photoresist according to the pattern of the mask. Afterwards, the uncured polymer is removed (D in Figure 2.4), thus the master is completed and ready for the preparation of several elastomeric stamps. A poly(dimethylsiloxane) (PDMS) elastomer is typically used as a stamp to transfer the pattern from the master to the substrate. For the stamp preparation, a liquid vinyl-

terminated prepolymer and the curing agent are mixed and the mixture is poured onto the patterned template. After curing the PDMS at 60°C, a solid elastomeric polymer is formed. Finally, the PDMS is peeled off, cut in proper size and used for the actual  $\mu$ -contact printing.<sup>55,56</sup>



**Figure 2.4:** Schematic illustration of the stamp preparation for  $\mu$ -contact printing by photolithography

Afterwards, the stamp will be loaded with the material that is to be printed, whereas the binding of the molecules to the new surface must be more energetically favourable, than staying on the stamp. According to the highly hydrophobic properties of PDMS only apolar materials can be used as ink solutions. For patterned surface properties, the most common ink solution that has been widely used is a thiol solution. Thiol solutions are SAM forming molecules, which allow the formation of a stable condition of molecules on the surface.



**Figure 2.5:** Schematic illustration of the actual  $\mu$ -contact printing

The inking of the stamp is either achieved by immersing the stamp in the ink solution or placing a droplet of the ink solution on the patterned side of the stamp (G in Figure 2.5). Afterwards, the stamp surface is dried by solvent evaporation in a nitrogen gas flow.<sup>59,56</sup> Then, the inked stamp is brought into contact with the gold surface (H in Figure 2.5) and the thiol is transferred to the surface (I in Figure 2.5). During this process, the thiol is selectively transferred to the surface according to the pattern of the stamp, as only the areas with the protrusions of the PDMS stamp are able to contact the gold surface.<sup>56</sup> After some time the stamp was separated carefully from the gold surface. For the SI-ATRP reaction prints a bifunctional

initiator that contained a thiol at one end and the ATRP initiator at the other end (a bromoisobutyrate moiety) was used.

For the use of patterned substrates for polymerization by ATRP, the patterned surface is backfilled with a different thiol, to allow the formation of a stable condition of a SAM on the whole gold surface (J in Figure 2.5). When the  $\mu$ -contact printing was realized with a thiol solution of molecules with terminal ATRP initiator, the unfilled surface areas of the gold surface are filled by a self-assembled monolayer of a thiol without a terminal ATRP initiator group, for example 1-octadecanethiol (ODT). This thiol has nearly the same length but a different head group which exhibits another surface chemistry. For the preparation of a SAM of the backfill thiol, the patterned gold-surfaces are exposed to a 1 mM thiol solution.<sup>60</sup> These patterned SAMs are ideally suited for grafting polymers onto surfaces because of the very high density of the functional groups, small number of defects and their well-defined structure. In addition, a systematic control of the spatial growth of polymer brushes on the surface is possible.

It has to be taken into account that undesired pathways for transport of thiols onto non-printed parts of the sample may exist. The transport of thiols through the stamp depends on the molecular weight of the thiol ink. Transport through the ambient air is proportional to the vapor pressure of the ink and vapor pressure decreases with increasing molecular weight.<sup>61</sup> A stamp deformation during stamp removal from the template and during the contacting of the substrate also has to be taken into account, which limits the resolution of the patterning.<sup>56</sup> But still this form of soft lithography technique always produces sharp boundaries between the distinct chemical regions on the substrate to be used for SI-ATRP polymerizations. This feature is useful for creating substrates with well-defined chemical patterns of polymer brushes.<sup>35</sup>

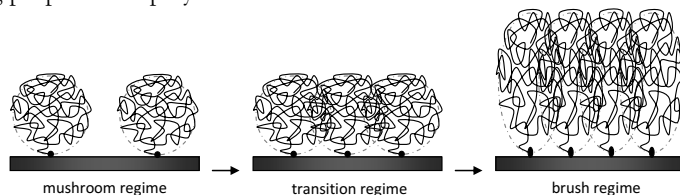


## 2.4 Variation of Polymer Brushes

Polymer brushes are a very attractive tool for tailoring interfacial properties and SI-ATRP is a very suitable synthesis strategy to grow these polymer brushes from a surface because it allows a good control over the brush thickness and grafting density.<sup>41,62</sup> In this case, the polymer layer thickness can be easily and precisely controlled by varying the polymerization time.<sup>60,63</sup>

### 2.4.1 Grafting Density

The variation of the grafting density is based on the modification of the substrate, more precisely on the resulting surface chemistry of a mixed SAM.<sup>52</sup> This approach focuses on covalently grafting thiol molecules onto the surface containing a defined amount of initiator moieties, whereas these macroinitiators are large compound molecules composed of both initiating and anchoring moieties.<sup>7</sup> The results of previous projects have shown, that the thickness of polymer brushes is linked to the initiator density on the gold substrate, which can be associated to the final polymer grafting density.<sup>62,64</sup> This aspect enables a new way to tune the thickness and the resulting properties of polymer brushes.



**Figure 2.6: Model of the varied grafting density of polymer brushes**

If the graft density of polymer brushes is high, the polymer chains tend to be strongly stretched along the direction perpendicular to the substrate (brush regime, Figure 2.6). In the case of low densities, the “mushroom” chain conformation similar to that of the free chains will appear for the tethered chains.<sup>65,66</sup> With increasing grafting density, the chains are more and more forced to a brush morphology as a result of a balance between an entropic effect, caused by higher orientation of the chains, and an energetic effect due to minimization of the repulsive interactions.<sup>24,45</sup> Also steric factors can inhibit the polymer chains growing from every single initiator molecule in the SAM. The surface average cross sectional area of an initiator molecule ( $20 \text{ \AA}^2$ ) is much smaller than the area of a polymer chain ( $\sim 180\text{--}200 \text{ \AA}^2$ ). In this case, only one out of 10 initiator molecules bound to the surface is expected to initiate a polymer chain.

### 2.4.2 Cross-linking Density

The variation of cross-linking density is based on the fractional feed of a cross-linker in the polymerization solution, which usually results in an insoluble three-dimensional polymeric gel.<sup>29</sup> Polymer gel brushes were previously prepared either in situ, by surface initiated polymerization in presence of a cross-linker, or ex situ by postmodification of presynthesized polymer brushes.<sup>12,29, 67</sup> The surface grafted polymer networks represent a novel class of thin hydrogel films (covalently cross-linked hydrogel brushes), whereas the ability to introduce and modulate the cross-linking density within surface grafted polymer brushes is expected to influence their mechanical and chemical stability, permeability and swelling characteristics. The change of lateral forces upon cross-linking depends on the dissociation kinetics of the cross-linkers, which therefore provide a molecular handle to control the mechanical properties of surface grafted polymer brushes.<sup>67</sup>

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Cross-Linking Density via SI-ATRP

Analysis of the Mechanical Properties by AFM

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