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Functionalization of Surfaces Using Polymer Brushes: An Overview of Techniques, Strategies, and Approaches

Juan M. Giussi, M. Lorena Cortez, Waldemar A. Marmisollé, and Omar Azzaroni

Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Universidad Nacional de La Plata, CONICET, La Plata, Argentina

1.1 Introduction: Fundamental Notions and Concepts

From an historical perspective, much of the interest in chemical modification of surfaces originated from their importance to different technologies, namely wetting, adhesion, catalysis, lubrication, detergency, biocompatibility, corrosion, or colloidal stabilization, among other examples.[1–3]

During the early years, when sophisticated spectroscopies working under ultrahigh vacuum conditions were developed, the central interest of surface science was especially focused on unraveling the atomic and electronic structures of metals, metal oxides, and semiconducting surfaces (usually as single crystals). However, by the end of past century, with the advent of new chemical techniques to integrate functions on solid substrates, surface science started to look at organic surfaces as ideal partners to address emerging and challenging issues on the technological agenda, for example, in relation to the development of antifouling biocompatible coatings for biomedical devices or the rational design of antifogging coatings with frost-resisting capabilities for the automotive industry.

The controlled transfer of organized monolayers of amphiphilic molecules from the air–water interface to a solid substrate was the first molecular-scale technology for the rational design of organic surfaces, this being a technology designed by Langmuir and Blodgett in the 1930s.[4,5] Later on, Levine and Zisman studied the physical properties of monolayers adsorbed at the solid–air interface and their effects on friction and wettability.[6] However, a new element came into play in the early 1980s with the discovery of self-assembled

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monolayers (SAMs).[7,8] SAMs provided a method to create organic surfaces with known, reproducible structures. Alkanethiolate SAMs definitively shifted the focus of surface science from metals and metal oxides to surfaces constituted of organic molecules and allowed studies of biologically relevant surfaces. The ability to control the composition of the surface made it possible not only to examine structure–property relationships, but, which is more important, to design and prepare surfaces displaying functions relevant in materials science, nanoscience, and biology.

Despite the versatility of these systems, one important limitation of SAMs is that functional groups can only be introduced at the surface. This means that SAMs by themselves cannot generate functional three-dimensional (3D) interfacial architectures—this being a decisive factor in multiple contemporary applications of organic thin films. In light of this context, polymer brushes gradually emerged as major players in different technological areas demanding new approaches for surface modification.[9–12] Polymer brushes refer to assemblies of macromolecules that are tethered by one end to a surface or interface and can be generated through different strategies. Bringing polymeric building blocks—in the form of polymer brushes—into the game opens a new dimension: Chemical groups can be carried all along the polymer backbone and can be placed in different pseudo-3D spatial arrangements when multiblock polymers are used.

The most prominent difference between SAMs and polymer brushes is the dimension of the building blocks themselves: SAMs are constituted of assemblies of small molecules, whereas polymer brushes are constituted of polymeric chains. The use of macromolecular building blocks brings in functional versatility but also introduces structural complexity that depends on the grafting density of the tethered polymer chains. For example, the entropic cost for polymer brushes to stretch out to their maximum length is very high and, consequently, polymer brushes are disordered at the molecular level. At very low grafting density, the so-called "mushroom regime," the polymers adapt a more or less random coil conformation (see Figure 1.1).[13] In good solvents, the thickness of the anchored polymer, H, in the mushroom regime (low grafting density) scales as $H \propto N\sigma^0$, where N is the degree of polymerization of the polymer and σ is the grafting density. The grafting density (σ) is defined by $\sigma = (H\rho N_\mathrm{A})/M_n$(where H, brush thickness; ρ, bulk density of the brush composition; N_A, Avogadro's number; and M_n molecular weight of the tethered polymer chains). Upon increasing the grafting density, polymer chains interact with each other and there will be a degree of distortion from the random coil. At sufficiently high grafting density, the so-called brush regime is reached (Figure 1.1). In this regime, the brush height scales as $H \propto N\sigma^{1/3}$. These simple scaling laws connecting grafting density and molecular weight (or degree of polymerization) with brush height were first derived by Alexander[14] and de Gennes[15] and then corroborated experimentally by different authors.

The overlap between the chains and the degree of stretching is heavily dependent on the grafting density, the chain length (or the degree of

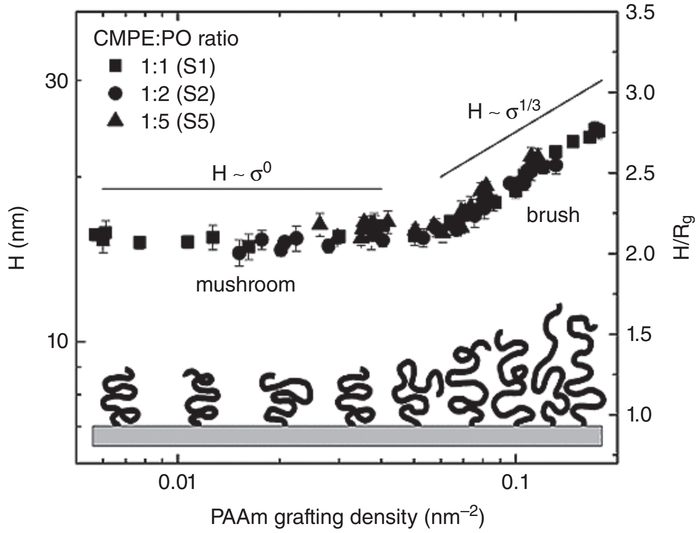

Figure 1.1 Wet thickness of polyacrylamide (PAAm) films as a function of the PAAm grafting density. Samples prepared on substrates containing the initiator gradients made of 1-trichlorosilyl-2-(*m*/*p*-chloromethyl phenyl) ethane: octadecyltrichlorosilane (CMPE: OTS) mixtures (w/w) 1:1 (squares), 1:2 (circles), and 1:5 (triangles). The inset shows a cartoon illustrating different polymer states with increasing grafting density. *Source*: Wu et al. 2003.[13] Reproduced with permission of American Chemical Society.

polymerization), and the solvent quality. In good solvents, the chains swell forcing them to stretch away from the surface. The extent of stretching is governed by a competition or interplay between the entropic loss due to chain stretching and the excluded volume interactions between different segments of the tethered polymer chains.

If the excluded volume interaction can be altered, then the conformation of the chains will, in turn, change. As a result, polymer brushes experience swelling and collapse transitions in good and poor solvents, associated with large conformational changes of the polymer backbones. The conformational behavior of polymer brushes can become even richer when charges are introduced into the monomer units of the polymer backbone, that is, polyelectrolyte brushes. Pioneering works by Pincus[16] and Zhulina et al.[17] revealed the existence of different regimes for polyelectrolyte brushes in which the brush height was correlated with different parameters such as salt concentration, length of the polymer chains, grafting density, and degree of charging.

The above-mentioned notions reveal that the grafting density plays an important role in establishing the regime in which the macromolecular system operates, that is, "mushroom" or "brush" regime (Figure 1.1).[13] In many cases, for simplicity of expression, the term "polymer brush" is used as a synonym of the terms "tethered polymer chains" or "end-grafted polymers." However, strictly speaking, the term "polymer brush" should be associated with a layer of tethered polymer chains under specific conditions—when the behavior of the tethered layer is dictated by strong interactions between densely grafted polymer chains. A more detailed discussion of the definition of "polymer brushes" can be found in Brittain and Minko.[18]

1.2 Preparation of Polymer Brushes on Solid Substrates

The chemical and structural properties of thin polymer films are determined through the choice of monomer, surface attachment method, and polymerization conditions. Two general approaches are commonly employed to fabricate thin polymer films bound to a chosen substrate: "grafting to" and "grafting from" as shown in Figure 1.2. In the "grafting-to" technique, presynthesized polymers

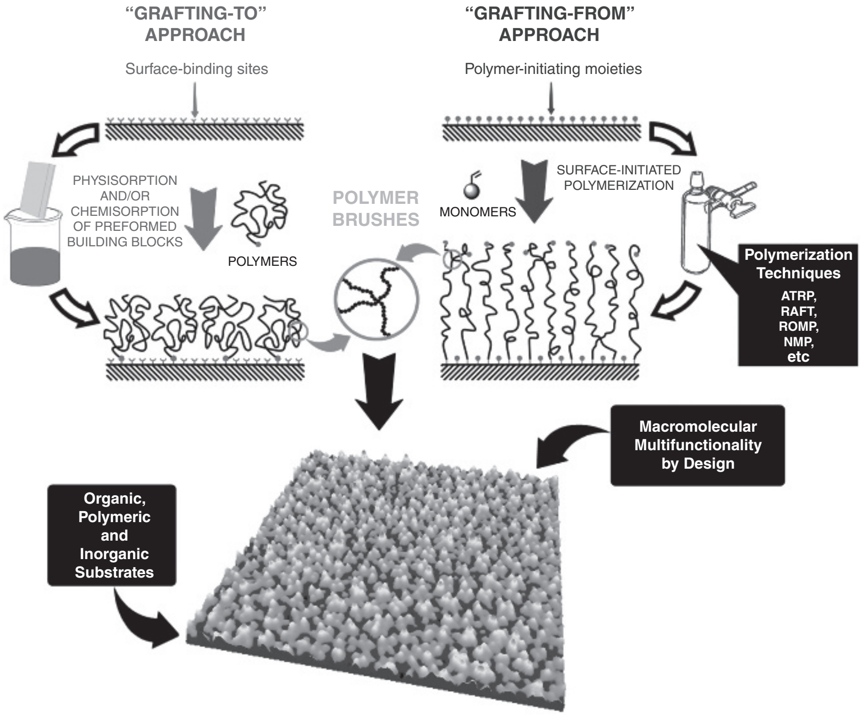

Figure 1.2 Conceptual illustration of the chemical strategies (grafting-to and grafting-from approaches) used to tether functional polymer brushes on a wide variety of substrates. The figure also includes an atomic force microscopy image (500 × 500 nm^2) of poly(2-(methacryloyloxy)-ethyl-trimethyl-ammonium chloride) brushes grown on silicon substrates via SI-ATRP. *Source*: Azzaroni 2012.[9] Reproduced with permission of Wiley-VCH Verlag GmbH & Co. KGaA.

are anchored to a surface from solution. On the other hand, the "grafting-from" method involves sequential growth of polymer chains from a surface.[19] The ability of low molecular weight monomers to diffuse to surface-active sites more readily than preformed macromolecules is the key concept, which differentiates the two approaches that we will discuss in the following sections.

1.3 Preparation of Polymer Brushes by the "Grafting-To" Method

The "grafting-to" approach is based on the chemical reaction between presynthesized polymers and reactive groups on the substrate, usually via an end functionality designed into the macromolecule. This chemical reaction can take place in a solution or in a melt. One of the attractive features of the "grafting-to" method is that it does not involve elaborate synthetic procedures. However, typical thickness values obtained by this technique are rather low, which is often considered a significant disadvantage of the method.

During a grafting-to procedure, macromolecular diffusion through a developing film rapidly encounters significant steric hindrance. As a result, many surface-active sites remain uncoupled and only thin, low-density polymer films can be achieved. In other words, "excluded volume" effects become more pronounced as the thickness of the polymer layer increases.[20] Karim et al.[21] argued that homogeneous, dense layers can be obtained readily in a poor solvent, because the steric interchain repulsion is diminished and the volume occupied by a polymer chain is smaller. This would allow other chains to reach the substrate more easily. This concept then led to the crucial task of devising new approaches for producing thicker grafted layers by minimizing the excluded volume interactions. These new strategies were based on the use of polymer melts,[22] or grafting from a concentrated polymer solution[23,24] and enabled the modification of flat[25–27] and porous[28] substrates, fibers,[29–31] and nanoparticles[32,33] using "grafting-to" techniques.

The "grafting-to" approach has also been used for creating polymer brushes with variations in grafting density along a substrate—the so-called "gradient polymer brushes." This type of film architecture can be obtained either by inducing a gradient in the grafting temperature in order to exploit the temperature dependence of grafting kinetics[34–36] or by methods based on gradual controlled immersion of the substrate into a solution of the reactive polymer in order to control the time of the grafting reaction.[37]

One of the most important aspects of the "grafting-to" process is its direct link to the surface chemistry of the employed substrate, as it governs four key elements: (i) the compatibility of the method with the surface that we are intending to modify, (ii) the processing conditions, (iii) the maximum grafting density of the layers that can be obtained, and (iv) the chemical stability of the tethered polymer layers.

In many cases, this method demands the preconditioning of the substrates in order to introduce the desired complementary functional groups for the grafting reaction. To this end, several groups explored a variety of strategies for surface preparation and priming, including plasma treatments,[38] chemisorption of SAMs,[39] and deposition of reactive polymer layers,[40] among others.

Among different approaches for surface preparation, the use of SAMs represents one of the most popular strategies to introduce predesigned reactive functional groups onto the most frequently used working substrates, Au and SiO_2/Si.

In the case of gold substrates, thiol chemistry has been extensively used for attaching a broad variety compounds with the thiol (–SH) terminal groups to gold substrates.[41] On the other hand, the use of silane chemistry is the preferred strategy to modify not only SiO_2/Si surfaces but also oxide surfaces.[42]

The introduction of thiol groups in the polymer structure permits the facile modification of gold substrates via a “grafting-to” approach. The strategy has been used to prepare polystyrene (PS),[43,44] polyethylene oxide,[45,46] poly(*N*-isopropylacrylamide),[47,48] poly[(2-dimethylamino)ethylmethacrylate],[49] and xyloglucan[50] brushes by simple chemisorption of thiol-terminated polymer chains on the gold substrate. Moreover, an alternative and complementary approach was also envisaged making use of the reduction of the dithioester end group of a polymer synthesized via reversible addition–fragmentation chain transfer (RAFT) polymerization. This strategy has been employed to generate mixed brush layers on gold nanoparticles by reducing gold precursors in the presence of RAFT-synthesized PS and poly(*N*-isopropyl acrylamide) (PNIPAM) polymers.[48]

The “grafting-to” modification of SiO_2/Si substrates using silane chemistry can be accomplished through different strategies. Rafailovich and co-workers[26] resorted to $Si(OH)_3$-terminated PS for the preparation of polymer brushes via a “grafting-to” method. End-functionalized polymers were spun onto Si substrates, and samples were then vacuum annealed at 170°C for 3 days in order to ensure enough mobility for the chain ends to reach the grafting surface, where they were chemically reacted via silane chemistry to form 5-nm-thick PS brushes. Different grafting densities were obtained by dipping the samples in toluene for different times subsequent to film deposition. As a result, the grafting density decreased upon increasing the duration of the immersion. In a similar vein, the grafting of tri-ethoxysilane-terminated PS onto silicon substrates from a melt was thoroughly investigated by Jones and co-workers.[20] These authors observed that the initial film thickness of the spun-cast layer and the polymer molecular weight have a strong influence on the properties of the final grafted layer. In the case of PS brushes grafted via very reactive trichlorosilane end groups, Karim et al.[21] have shown that the morphology of the grafted layer was dependent on the grafting time. Short reaction times gave rise to a grafted layer exhibiting an inhomogeneous island-like structure. Upon increasing the reaction time, the island-like structures increased in size and for sufficiently long grafting times homogeneous films were obtained. According to these authors, the random deposition of the reactive polymer chains on the substrate was the main mechanism responsible for the morphological evolution of the film.

Another particularly interesting approach to tether polymer layers using a "grafting-to" method is to take advantage of the chemical reactivity of epoxy groups. The high reactivity of this functional group is due to the high tension in the three-membered epoxide ring as well as to the polarity caused by the oxygen atom. Through this strategy, different authors reported the preparation of grafted polymer layers by reacting epoxy groups with (i) carboxyl groups,[51–58] (ii) amino groups,[37,59–63] (iii) thiols groups,[64] and (iv) maleic anhydride.[65,66] The formation of covalent bonds between surface-confined moieties and functional groups in the polymer chains has also been extended to the exploration of quaternization reactions as synthetic routes. In this regard, alkylation of polymers bearing pyridine rings in the presence of surfaces exposing halogen atoms has been investigated by Minko and co-workers as a method to prepare stable polymer layers.[67,68]

In some cases, substrates are preconditioned by simple adsorption of an anchoring polymer layer ("primer") onto the working surface. As an example, Nnebe and Schneider reported the use of physisorbed poly(ethyleneimine) as a strategy to functionalize silica surfaces with amino groups which would then be employed to graft succinimidylpropionic acid-derivatized polymers.[69] However, when using physisorbed "primers," the stability of the grafted layer could be compromised leading to film desorption in the presence of different environmental variables such as solvent, ionic strength, or temperature. The stability of the priming layer can be enhanced by resorting to chemisorption instead of physisorption. In this configuration, after the chemisorption process, the priming layer exposes reactive segments located in the "loop" and "tail" domains of the anchored polymer chains that are not linked to the substrate.[70] One typical example of chemisorbed polymeric primers is the case of polymers bearing epoxy groups. An interesting investigation carried out by Köthe et al.[40] revealed that surface hydroxyl groups exposed on oxide surfaces are reactive enough to form chemical bonds with adsorbed epoxidized polybutadiene layers. This experimental observation permitted further substrate modification by diisocyanate- and amino-terminated polymers.

With regard to this subject, special attention has been given to the use of poly(glycidyl methacrylate) (PGMA), where an epoxy group is present in each monomer unit, as a macromolecular primer compatible with different "grafting-to" chemistries (Figure 1.3). Extensive work by Luzinov and his collaborators on this topic demonstrated that uniform and homogeneous

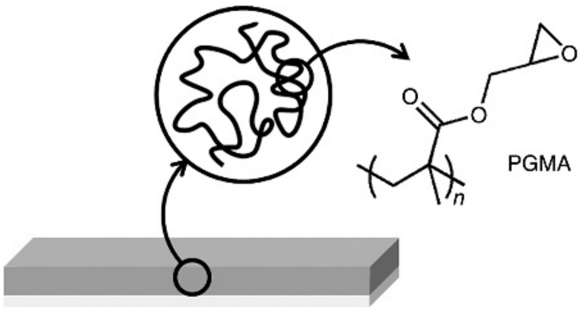

Figure 1.3 Schematic depiction of the macromolecular anchoring layer constituted of PGMA.

epoxy-containing polymer layer can be deposited onto various surfaces by adsorption, spin coating, or dip coating.[71–74]

By way of example, Iyer et al.[75] demonstrated that carboxylic acid- and anhydride group-terminated PS polymer chains can be grafted onto PGMA-modified silicon wafers yielding dense and homogeneous layers. PS films were dip-coated from toluene solution onto wafers modified with a PGMA anchoring layer. Samples were then annealed during 18 h in a vacuum oven preheated to 150°C to enable the end groups to react with the epoxy-modified substrate. The same group also demonstrated the effective tethering of polyethylene glycol (PEG) layers from a melt onto PGMA primers using a similar "grafting-to" approach.[71,73] These authors observed that the maximum grafting amount was limited by the concentration and availability of epoxy groups in the PGMA layer chemisorbed to the substrate. As expected, the grafting density of the tethered PEG layers was dependent on the molecular weight of the polymer chains.

The use of a macromolecular PGMA platform also provides an interesting avenue to create mixed polymer brushes consisting of two or more incompatible polymers grafted onto the same substrate. One of the key advantages of this approach relies on the thermal stability of epoxy groups that enables the sequential grafting of different end-functionalized polymer onto the same substrate. In this way, a number of research groups devised the construction of "responsive" surfaces exposing either hydrophobic/hydrophilic or anionic/cationic mixed brushes through the sequential grafting onto PGMA layers.[76–79]

Another interesting strategy to graft polymers on PGMA layers is by using the technique called "solvent-assisted grafting."[80] This technique enables the tethering of polymer layers at relatively low temperatures (20–40°C) and is based on the saturation of the polymer film to be grafted with solvent vapor. In this way, the solvent present in the deposited polymer layer not only acts as a plasticizer reducing the glass transition temperature but also decreases the polymer layer viscosity which, in turn, enhances the mobility of the polymer chains at the interface. As a result, due to the enhanced interfacial mobility the "solvent-assisted grafting" technique can yield, under mild conditions, grafting densities comparable to those obtained during melt grafting.

1.4 Polymer Brushes by the "Grafting-From" Method

1.4.1 Surface-Initiated Atom Transfer Radical Polymerization

Atom transfer radical polymerization (ATRP) represents one of the most popular techniques for the formation of polymer brushes through surface-initiated polymerization. One of the most appealing aspects of ATRP is its chemical versatility and robustness to grow a variety of monomers. The technique was developed in the mid-1990s,[81–83] and since then it has been employed to grow different types of polyelectrolyte and polymer brushes. This polymerization technique relies on the reversible redox activation of a "dormant" alkyl halide terminated polymer chain end by a halogen transfer to a transition metal complex (Figure 1.4). This process leads to the homolytic rupture of the carbon–halogen bond, thus generating free radical species at the polymer chain end. This activation step involves an electron transfer from the transition metal complex to the halogen atom, which, in turn, leads to the oxidation of the transition metal complex. Concomitantly, upon increasing the concentration of the oxidized form of the catalyst, the equilibrium is displaced toward the formation of halogen-capped dormant species. Due to the complex interplay between the different species involved in the polymerization process, the rate and the extent of the ATRP reaction are highly dependent on different parameters, such as catalyst concentration, type of ligand, solvent, and initiator.[84]

One of the first attempts to grow polymer brushes via surface-initiated atom transfer radical polymerization (SI-ATRP) was reported by Huang et al. involving the grafting of poly(acrylamide) (PAM) brushes from a self-assembled benzyl chloride monolayer on silica gel using Cu(bpy)$_2$Cl to control the radical population.[85]

Later on, Fukuda and co-workers employed 2-(4-chlorosulfonylphenyl)ethyl silane SAMs deposited via the Langmuir–Blodgett technique to grow poly(methyl methacrylate) (PMMA) brushes.[86] In order to control the

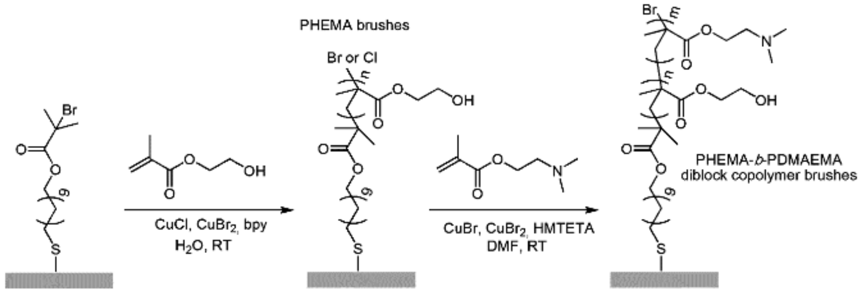

Figure 1.4 Scheme describing the preparation of poly(2-hydroxyethyl methacrylate)-*block*-poly(dimethylaminoethyl methacrylate) (PHEMA-*b*-PDMAEMA) diblock copolymer brushes via SI-ATRP from 2-bromoisobutyrate-terminated SAMs chemisorbed on gold surfaces.

polymerization, these authors added *p*-toluenesulfonyl chloride as a sacrificial initiator. In many cases, an alternative strategy to achieve a controlled polymerization is to add Cu^{II}—or the metal ion in the oxidized form—directly to the polymerization solution. Using this versatile strategy, Matyjaszewski and co-workers demonstrated the controlled living polymerization of PS brushes from silicon substrates bearing bromoisobutyrate moieties.[87]

The solvent also plays an important role in tuning the performance of SI-ATRP. Different authors reported a marked increase in the polymerization rate in the presence of polar solvent, being this effect more drastic in the case of aqueous solvents.[88–90] By way of example, we can mention that Jones and Huck were able to grow 50-nm-thick PMMA brushes in a controlled manner within 4 h of reaction time using a water/methanol mixture as a polymerization medium.[91]

In a similar fashion, the combination of different catalyst and deactivator species in the presence of aqueous solvents can facilitate the tuning of the polymerization reaction. Bruening and co-workers reported the synthesis of 700-nm-thick poly(2-hydroxyethyl methacrylate) (PHEMA) brushes using a mixed halide $Cu^{I}Cl/Cu^{II}Br_2$/bpy catalyst into aqueous medium.[92] The success of this strategy based on mixed halide systems relies on the higher free energy of dissociation of the C–Cl bond as compared to the C–Br bond. As a consequence, this difference between halide systems is translated into a displacement of the equilibrium between dormant and propagating radical species toward the formation of dormant species, thus increasing the control over the polymerization reaction.[93]

In order to reduce the amount of catalyst used in the ATRP reaction, Matyjaszewski and his collaborators have introduced an interesting variation to the traditional ATRP that allows not only to reduce the concentration of the copper catalyst to a few parts per million but also to increase the tolerance toward the presence of oxygen in the polymerization solution. This technique is known as "activators (re)generated by electron transfer" ATRP or Activators ReGenerated by Electron Transfer (ARGET) ATRP[94,95] and involves the use of reducing agents such as ascorbic acid, or even metallic Cu(0), to reconstitute Cu^{I} from Cu^{II} in solution and activate the surface-initiated polymerization.[96–101]

1.4.2 Surface-Initiated Reversible-Addition Fragmentation Chain Transfer Polymerization

RAFT polymerization is a controlled/living polymerization technique in which chain growth is initiated using a free radical initiator, for example, azobisisobutyronitrile (AIBN), and mediated by a chain transfer agent (CTA) constituted of dithioester, dithiocarbamate, or trithiocarbonate compounds. In this technique, radical transfer between growing chains is responsible for providing good control over the polymerization process. Concomitantly, the "capping"

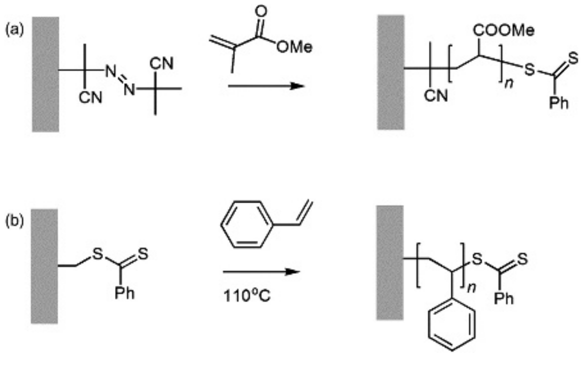

Figure 1.5 Scheme describing the preparation of polymer brushes through RAFT polymerization: (a) poly(methylmethacrylate) and (b) polystyrene.

of growing chains by the dithioester moiety confers good living characteristics to the polymerization reaction (Figure 1.5).

In most cases, the generation of polymer brushes via RAFT polymerization involved the use of either surface-immobilized conventional free radical initiators or surface-immobilized RAFT agents.

One of the first attempts to grow brushes using surface-initiated reversible-addition fragmentation chain transfer polymerization (SI-RAFT) was reported by Baum and Brittain using silicon substrates modified with SAMs bearing azo initiator groups in the presence of a dithiobenzoate CTA.[102]

These studies revealed that small amounts of untethered radical initiator, for example, AIBN, dissolved in solution were necessary for surface-initiated polymerization to be accomplished. The authors hypothesized that the addition of initiator in solution was required to scavenge impurities that quickly terminate growing chains. It is worth noting that the presence of free initiator in solution also increases the amount of radicals in the systems, which are necessary to avoid early termination by CTA capping. However, the drawback of this approach relies on the fact that the surface reaction takes place in parallel with polymer growth in solution and consequently brush-modified samples must be extensively washed with a solvent before performing any characterization. One of the interesting features of this technique is that, even though the polymerization is rather slow, it is highly living. In this context, the same authors demonstrated that the reinitiation of the polymer chains permitted the growth of block copolymer brushes of PS-*b*-PDMA (polystyrene-*block*-poly(*N*,*N*-dimethylacrylamide)) and PDMA-*b*-PMMA (poly(*N*,*N*-dimethylacrylamide)-*block*-poly(methyl methacrylate)), and the sequential reinitiation of chains with the same monomer multiple times.

Thereafter, different groups employed this strategy to grow poly(chloromethylstyrene) (PCMS),[103] poly(pentafluorostyrene),[103] poly(sulfobetaine methacrylate),[104] poly(sodium 4-styrenesulfonate) (PSS-(Na)),[104] PMMA,[105] poly(poly(ethylene glycol) methyl ether methacrylate),[105] and poly(2-(dimethylamino) ethyl methacrylate) (PDMAEMA)[105] brushes from azo-functionalized substrates.

On the other hand, instead of performing SI-RAFT using free radical initiator-modified substrates, several research groups explored the synthesis of polymer brushes using surface-immobilized RAFT agents. In general, RAFT agents can be immobilized according to two synthetic approaches: the R-group and Z-group approaches (Figure 1.6). The R-group approach refers to a configuration in which the RAFT agent is tethered to the surface through the leaving and reinitiating R group. This approach has been successfully employed to grow polymer brushes from a variety of dithiobenzoate- or trithiocarbonate-modified substrates, including silicon wafers,[106–108] silica particles,[109–112] CdSe,[113] and gold[114] nanoparticles, and multiwalled carbon nanotubes.[115–117]

The Z-group approach (Figure 1.6) refers to the anchoring of the RAFT agent via the stabilizing Z group and has been employed to prepare a variety of

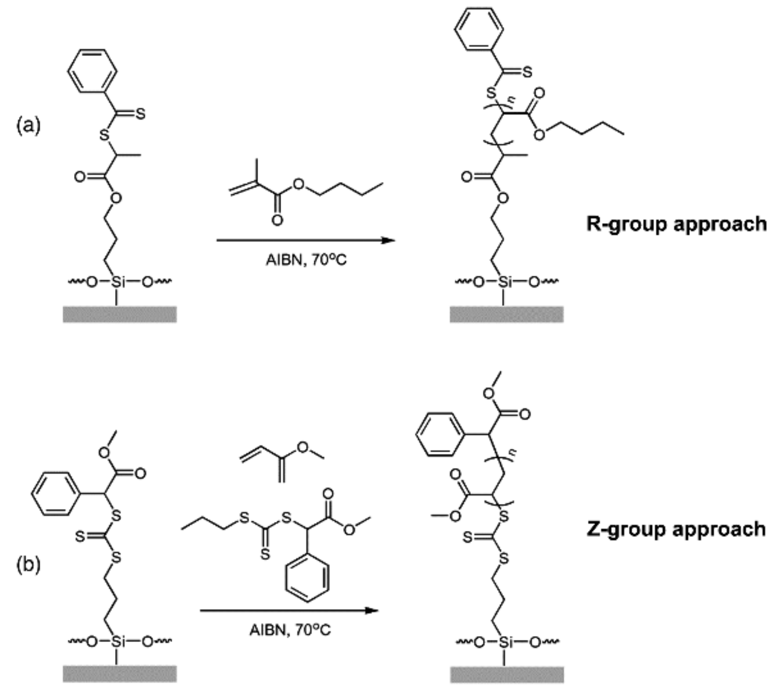

Figure 1.6 (a) Scheme describing the SI-RAFT polymerization of poly(butyl acrylate) brushes from dithiobenzoate-modified silica surfaces via a R-group approach. (b) Scheme describing the SI-RAFT polymerization of poly(methyl acrylate) brushes from silica surfaces modified with trithiocarbonate derivatives via a Z-group approach.

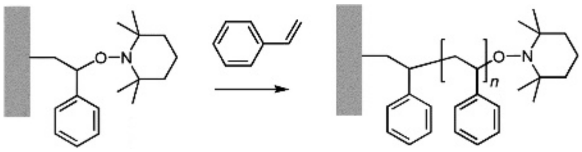

Figure 1.7 Scheme describing the synthesis of PS brushes nitroxide-mediated polymerization.

polymer brushes constituted of methacrylic, acrylic, styrenic, and acrylamide-based monomer units.[118–124]

1.4.3 Surface-Initiated Nitroxide-Mediated Polymerization

Nitroxide-mediated polymerization constitutes a living polymerization technique based on the reversible capping of an active chain-end radical with a nitroxide leaving group. The first successful implementation of this technique to synthesize polymer brushes was reported by Husseman et al.[125] These authors employed silicon wafers modified with bound alkoxyamine initiator molecules to grow PS brushes—ca. 100 nm in thickness after 16 h of polymerization. The strategy to grow the polymer brushes relies on heating the initiator-functionalized wafer to 120°C, in order to cleave off the alkoxyamine moiety with the subsequent release of an alkyl radical and the stable nitroxide radical, (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO) (Figure 1.7). The propagation is controlled by the reversible "capping" of the growing chain by the TEMPO radical, thus conferring a "living character" to the polymerization (Figure 1.7). In most cases the use of surface-bound initiators alone is not sufficient to attain a controlled polymerization. The very small number of growing polymer chains, as compared to the monomer concentration, gives a very low overall concentration of free TEMPO, which in turn leads to inefficient capping of chain ends. One of the most common strategies to solve this problem is to add a "free" alkoxyamine initiator to the polymerization solution. However, this route can also lead to the formation of polymer in solution which must be removed from the brushes by extensive rinsing with solvent before further characterization.

Since then, surface-initiated nitroxide-mediated polymerization was employed by different research groups for growing different polymer brush systems such as poly(3-vinylpyridine),[126,127] poly(4-vinylpyridine),[128] PSS(Na),[128] and poly(4-(poly(ethylene glycol) methyl ether)styrene) brushes,[129] from a variety of TEMPO-functionalized substrates.

1.4.4 Surface-Initiated Photoiniferter-Mediated Polymerization

Surface-initiated iniferter-mediated polymerization is a technique based on the use of a special type of initiators called "iniferters." These iniferters are

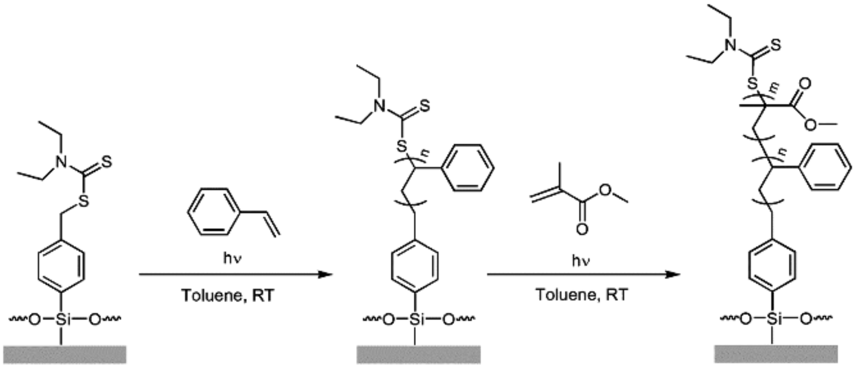

Figure 1.8 Scheme describing the preparation of polystyrene-*block*- poly(methyl methacrylate) (PS-*b*-PMMA) brushes through SI-PIMP from a benzyl-*N*,*N*-diethyldithiocarbamate-derivatized SiO_2/Si substrate.

molecules displaying singular characteristics provided that they can simultaneously act as initiators, transfer agents, and terminators. In general, dithiocarbamate derivative molecules are capable of acting as photoiniferters as they can initiate upon exposure to light and act as transfer agents or terminators during polymerization. Upon exposure to UV light, the photoiniferter molecules undergo photolysis, yielding a carbon radical and a dithiocarbamate radical. While the carbon radical is reactive and can initiate polymerization by reacting with the monomers, the dithiocarbamate radical is stable and reacts weakly, also with the monomers.[130] However, and more important, the dithiocarbamate radical can reversibly terminate the propagating chains, thereby imparting the "living" characteristics to photoiniferter-mediated photopolymerization (Figure 1.8). In other words, upon photolysis the carbon radical undergoes addition of monomers to initiate the chain propagation and concomitantly the dithiocarbamate radical act as a transfer agent inducing reversible termination of the growing polymer chains (Figure 1.8). This interesting strategy was first proposed by Otsu et al. in the early 1980s, demonstrating that photoiniferter-mediated polymerization of methyl methacrylate (MMA) exhibits living characteristics, that is the molecular weight of the PMMA chains increased linearly with monomer conversion.[131,132] The same group then demonstrated that the living characteristics of this technique allowed for block copolymers of PS and PMMA to be synthesized, both in solution and on the surface of particles.[133]

Due to the photosensitive nature of the iniferter molecules, this polymerization technique is heavily reliant on the intensity of the irradiating light. As such, surface-initiated photoiniferter-mediated polymerization (SI-PIMP) can be spatially and temporally controlled by manipulating the location, intensity, and duration of UV irradiation.[134,135]

Along these lines, Matsuda and his collaborators extensively explored the use of SI-PIMP to synthesize different polymer brush systems, including poly(acrylic acid), PNIPAM, PCMS, poly(poly(ethylene glycol) methacrylate), poly(sodium methacrylate) (PMAA-(Na)), and poly(methacrylic acid) (PMAA), from substrates modified with benzyl-*N*,*N*-diethyldithiocarbamate-moieties.[136–140] Using a similar strategy, Hadziioannou and co-workers resorted to the use of a trimethoxysilane-appended benzyl-*N*,*N*-diethyldithiocarbamate iniferter to derivatize silicon substrates and then grow PS brushes.[141]

It is important to mention that some studies on the growth of MMA brushes revealed a pseudo-living behavior due to irreversible termination reactions. This effect ultimately leads to the loss of surface free radicals upon increasing exposure (or polymerization) time.[142] The nonlinear growth of the brush layer as a function of irradiation time was ascribed to bimolecular termination reactions, rather than chain transfer to monomer. To overcome this limitation, a strategy to increase the amount of deactivating species was proposed in order to attain a controlled radical polymerization behavior.[143,144] This strategy was based on the addition of tetraethylthiuram disulfide to the polymerization solution with the aim of deactivating the generated dithiocarbamyl radicals.

1.4.5 Surface-Initiated Living Ring-Opening Polymerization

The application of surface-initiated ring-opening polymerization (SI-ROP) as a strategy to graft polymer layers on modified substrates was first proposed by Jordan and Ulman in the late 1990s.[145] These authors exploited the capabilities of the living cationic ROP of 2-ethyl-2-oxazoline to produce linear poly(*N*-propionylethyleneimine) (PPEI) (Figure 1.9). The synthetic protocol to attain the polymer layers consisted of several steps. First, gold-coated substrates were modified with trifluoromethane sulfonate (triflate) moieties through the chemisorption of 11-hydroxyundecanethiol SAMs and their subsequent vapor-phase functionalization. Thereafter, reaction with 2-ethyl-2-oxazoline in refluxing chloroform for 7 days resulted in the formation of PPEI brushes of about 9 nm in thickness. Termination of the polymerization process was accomplished by the addition of *N,N*-dioctylamine, which in turn also generated amphiphilic brushes. This surface-initiated polymerization reaction does not require the presence of catalyst to produce well-defined brush layers; however, the brush growth is extremely slow as compared to catalyzed ring-opening polymerization (ROP).

Within this framework, Hawker and co-workers have used aluminum alkoxide catalyzed ROP to synthesize poly(ε-caprolactone) (PCL) brushes grafted from gold surfaces (Figure 1.9).[146] Di(ethylene glycol)-terminated SAMs were employed to expose OH groups for initiation, which resulted in good polymer growth reproducibility and long-term stability of the polymer layer. The

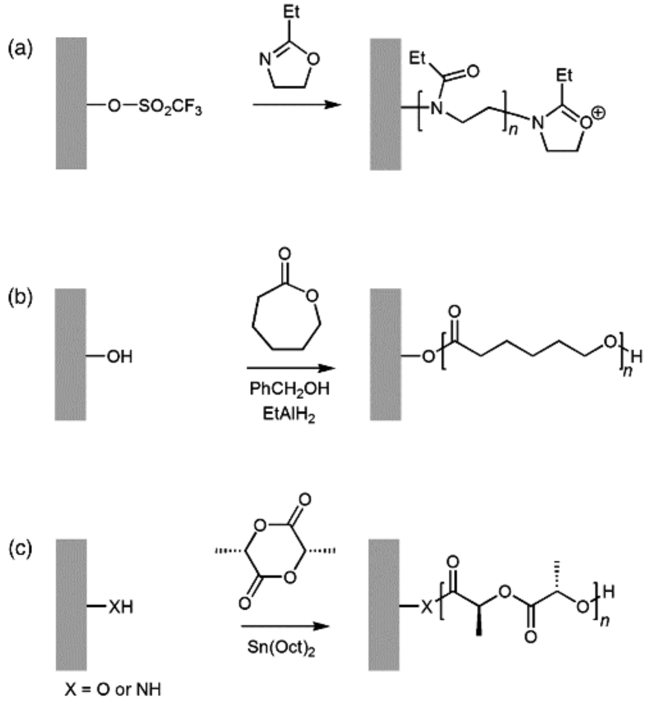

Figure 1.9 Scheme describing the preparation of different polymer brushes by living ROP: (a) poly(*N*-propionylethyleneimine), (b) PCL, and (c) PLA.

synthesis of the PCL brush layer was accomplished through organometallic catalysis in the presence of diethylaluminum alkoxides. The catalyzed SI-ROP process conducted at room temperature led to the formation of PCL brushes up to 70 nm thick in a few hours. It was observed that, in order to attain a good outcome of the surface-initiated process, it was necessary to add a free initiator (benzyl alcohol) to the polymerization solution. In this way, the brush thickness was controlled by the initial alcohol: ε-caprolactone ratio. The addition of free initiator in solution facilitates the exchange of the active site between bound and free polymer chains, thus promoting the establishment of adequate molecular weight control. However, this strategy leads to the generation of free polymer in solution that must be removed from the bound polymer brushes by rigorous solvent rinsing before proceeding to further work with the brush samples.

Later on, Choi and Langer reported the formation of chiral poly(lactic acid) (PLA) brushes grafted from gold and silicon substrates by ROP of L-lactide using tin(II) octoate as a catalyst (Figure 1.9). Depending on the nature of the substrate, these authors employed platforms of different chemical nature to grow the PLA brushes. In the case of gold substrates, the chosen platform was an oligo(ethylene glycol) terminated SAM that led to PLA brushes up to 12 nm thick after 3 days of reaction at 40°C. According to these authors, the thermal instability of thiol SAMs on gold precluded the use of higher reaction temperatures which could have led to the optimization of the polymerization reaction. However, the use of thermally stable amine-terminated SAMs on Si/SiO_2 surfaces enabled the use of much higher reaction temperatures, which ultimately permitted the formation of PLA brushes up to 70 nm thick after 3 days of reaction at 80°C without requiring free initiator in solution.

On the other hand, Wieringa et al. reported the growth of poly(L-glutamate) brushes from silicon and glass substrates modified with amine groups.[147] The proposed strategy involved the use of *N*-carboxy anhydrides of L-glutamates as monomers. These species are cyclized amino acids that undergo ROP in the presence of amine groups, thus leading to the formation of polyaminoacid brushes up to several tens of nanometers in thickness in only a few hours. The "living" nature of the polymerization technique was demonstrated by the reinitiation of the polymer chains, and the subsequent formation of diblock copolymer brushes.

1.4.6 Surface-Initiated Ring-Opening Metathesis Polymerization

Ring-opening metathesis polymerization (ROMP) is a variant of olefin metathesis chain-growth polymerization in which the driving force of the reaction is the relief of ring strain in cyclic olefins, for example, functionalized norbornenes. This polymerization technique takes place in the presence of metathesis catalysts to generate polymers from cyclic olefins. One of the first successful attempts to grow polymer brushes via surface-initiated ring-opening metathesis polymerization (SI-ROMP) was reported by Whitesides and co-workers in 2000.[148] The synthetic route relied on the use surface-grafted ruthenium catalysts to grow brushes from norbornene-based monomers on silicon substrates (Figure 1.10). The active surface bearing the catalytic sites was prepared by exposing norbornene-terminated trichlorosilane SAMs to a solution of Grubbs-type ROMP catalyst. Then, exposure to solutions of norbornene-based monomers prompted the rapid brush growth under controlled conditions, forming polymer layers up to 90 nm in thickness within 30 min. Further exposure of these brushes to a solution of a second monomer led the formation of diblock copolymer brushes, as revealed by infrared spectroscopy and ellipsometry.

A similar approach was also explored by Grubbs and co-workers to grow polymer brushes from silicon substrates using norbornene as a monomer.[149] Moon and Swager[150] used SI-ROMP to prepare poly(*p*-phenylene ethynylene) (PPE) brushes employing a norbornene-capped PPE macromonomer (Figure 1.10). The reaction conditions employed for the synthesis led to the formation

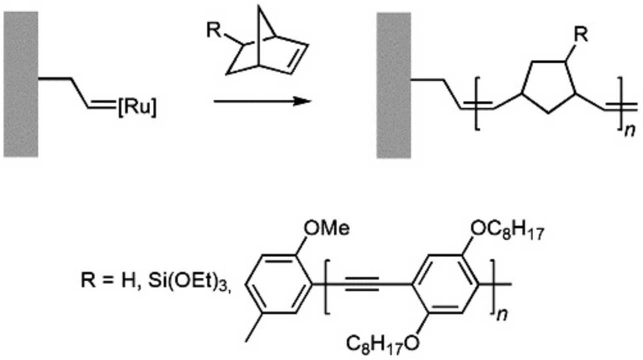

Figure 1.10 Polymer brushes grown by ring-opening metathesis polymerization of norbornene-derived monomers.

of 10 nm-thick PPE brushes and subsequent reinitiation in the presence of a mixture of 5-(bicycloheptenyl)-triethoxysilane, and the PPE macromonomer gave rise to 16 nm-thick diblock copolymer brushes.

1.4.7 Surface-Initiated Anionic Polymerization

Anionic polymerization is a polymerization technique that involves the polymerization of vinyl monomers in the presence of strong electronegative groups, and it is carried out through a carbanion-active species.[151,152] The initiation is triggered by species that undergo nucleophilic addition to the monomer. In most of the cases, the strength of the base used to initiate the polymerization depends on the monomer structure. The polymerization mechanism is based on the propagation of an ionic-active species, and consequently it is sensitive to the nature of the counterions in the reaction medium. The technique is very selective to the type of monomers that can be polymerized. This is due to the experimental fact that substituent groups should be able to stabilize the carbanions that are formed in the polymerization reaction. In general, monomers bearing substituents capable of stabilizing the carbanion through resonance or induction, for example, nitro, cyano, vinyl, phenyl, are compatible with anionic polymerization. In addition, the nature and purity of the solvent also play a critical role. In general, aprotic solvents can prevent transfer to solvent and termination. However, the presence of electrophilic impurities in the solvent can react with ionic sites and dramatically affect the polymerization.

In this context, Schouten and co-workers[153] explored the modification of silica surfaces with styrene groups and initiated the polymerization by activating the styrene units in the presence of *tert*-butyllithium. This strategy was extended to the formation of block copolymers of poly(styrene-*block*-isoprene)

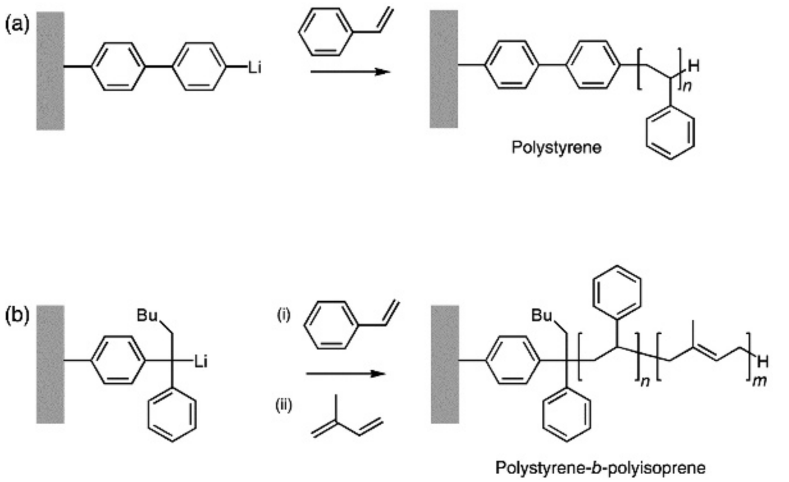

Figure 1.11 Scheme describing the preparation of different polymer brushes by living anionic polymerization: (a) polystyrene and (b) polystyrene-*block*-polyisoprene.

onto silica microparticles and glass slides (Figure 1.11). Several authors pointed out that a major limitation of this approach was the use of *tert*-butyllithium (*t*-BuLi) as an initiator for surface-initiated polymerization styrene in toluene.[154] This has been ascribed to the fact that *t*-BuLi initiation is very slow in nonpolar solvents, yielding broad molecular weight distributions. Ulman and co-workers explored the use of SAMs exposing biphenyllithium groups to initiate the anionic polymerization of styrene on gold substrates (Figure 1.11).[155] The bromobiphenyl groups were converted into initiating species by reaction with *sec*-butyllithium and subsequent addition of styrene led to the slow formation of uniform PS films reaching 18 nm in thickness after 3 days of polymerization. Then, Ingall et al.[156] demonstrated that anionic initiation of polymerization is also feasible using a bromopropyl trichlorosilane coupling agent to form the initial monolayer, followed by lithiation with lithium di-*tert*-butylbiphenyl. Using this approach, these authors were able to synthesize poly(acrylonitrile) brushes of ~245 nm in thickness.

On the other hand, Advincula and his collaborators explored an interesting alternative route based on the use of SAMs bearing 1,1-diphenylethylene (DPE) terminal groups as initiating sites for growing polymer brushes via surface-initiated anionic polymerization.[157–159] One of the most attractive advantages of using DPE is that it can react quantitatively with simple alkyllithiums to form a monoaddition product, a 1,1-diphenylalkyllithium initiating species.[160] These species are very reactive and serve as initiators for polymerization not only of styrenes and dienes in organic solvents but methacrylates and vinylpyridines at low temperatures in polar solvents such as tetrahydrofuran.[160] The same route has also been exploited by Quirk and co-workers to grow different polymer brush systems.[161,162]

The preparation of block copolymer brushes is also plausible through the use of DPE-terminated silane or thiol SAMs and the sequential addition of monomers. In a typical setting, the first reaction is allowed to reach completion and then the second monomer is added to the living chains, thus leading to the growth of the second block. This strategy has been employed by Advincula and co-workers to grow polystyrene-*b*-polyisoprene (PS-*b*-PI) and polybutadiene-*b*-polystyrene) (PBd-*b*-PS) block copolymer brushes on Au and SiO_2/Si substrates.[163]

1.5 Conclusions

The purpose of this chapter is to bring the reader up to date with the most recent experimental developments in relation to the preparation of polymer brushes—*the chapter was designed to give the reader the big picture*. We presented a general description of the synthetic approaches, focusing on some of the most relevant examples of the different synthetic strategies. It was our intention to lead the researcher through the vast literature in such a way that he or she will be able to pursue particular investigation with suitable guidance. In this context, we believe that carefully chosen references serve to guide the reader through the extensive literature, which makes the field accessible to a wide and varied audience including scientists, students, postdoctoral fellows, engineers, and industrial researchers. We hope that graduate students will find the chapter useful in their research and understanding of polymer brushes and beyond.

As summarized in Figure 1.12, a wide range of synthetic strategies have been employed for the preparation of polymer brushes on solid surfaces. Along the

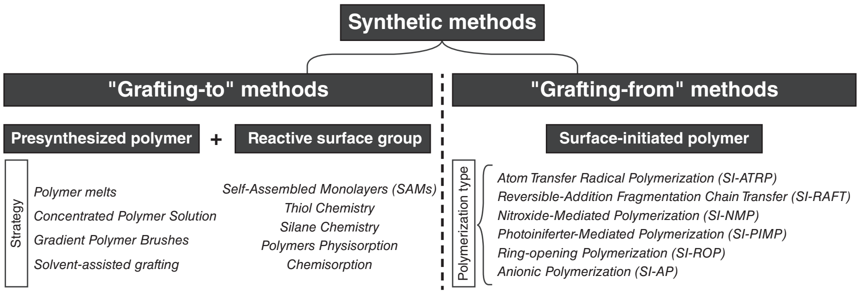

Figure 1.12 Synopsis of the main synthetic approaches for preparing polymer brushes.

different chapters of this book, we will see the importance of having at hand the most current techniques and procedures to tether polymer layers on different substrates. Polymer brushes offer an enormous infrastructure for a highly interdisciplinary integration of inorganic, organic, biological, and supramolecular systems on surfaces.

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