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Synthetic strategies to enhance the long-term stability of polymer brush coatings

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High-density, end-anchored macromolecules that form so-called polymer brushes are popular components of bio-inspired surface coatings. In a bio-mimetic approach, they have been utilized to reduce friction, repel contamination and control wetting, in particular in the development of biomedical materials. For reliable application of these coatings, it is critical that the performance of these coatings does not degrade in time. Yet, it is well-known that polymer brushes can deteriorate and degraft when exposed to water(–vapor) and this strongly limits the durability of these coatings. In this article, we provide an overview of the current status of research on the stability of polymer brushes. Moreover, we review different synthetic strategies, some of which are bio-inspired by itself, to enhance the long-term stability of these brushes. Based on this overview, we identify open question and issues to be resolved for brushes to be applied as durable bio-inspired surface coatings.

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1. Introduction

Polymer brushes consist of long macromolecules that are end-tethered to surfaces at sufficiently high densities such that the polymers stretch out, away from the substrate.[1,2] The advantage of end-anchoring of the polymers is that the coating can be utilized in good solvents, without being dissolved in the solvent. In the last decades, these brushes have been utilized in a multitude of bioinspired materials. For example, the strong swelling of brushes in good solvents can be utilized to mimic key elements of biological lubricants.[3–5] This has resulted in the development of highly effective synthetic lubricants.[6–8] Moreover, this strong brush swelling can be employed in the design of anti-fouling surfaces as well.[9–13] Other biomimetic materials, where polymer brushes have been incorporated, have been designed to display environmentally responsive[14–16] and structural[17–19] colours, as found in *e.g.* chameleons.[20] Next to these bioinspired approaches, brushes can also be applied in smart adhesives,[21,22] energy devices,[23,24] bactericidal[25–27] and blood compatible[28,29] coatings, membranes,[30,31] nano-theranostics,[32] sensing[33–35] and many more applications.[36–39]

End-anchored polymers can adopt different conformations. When the distance between the surface bonds is larger than two

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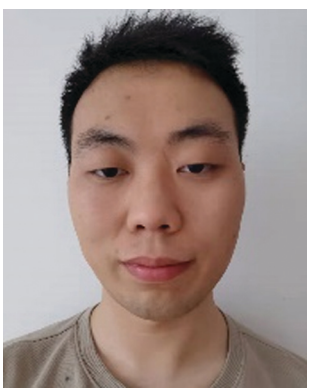

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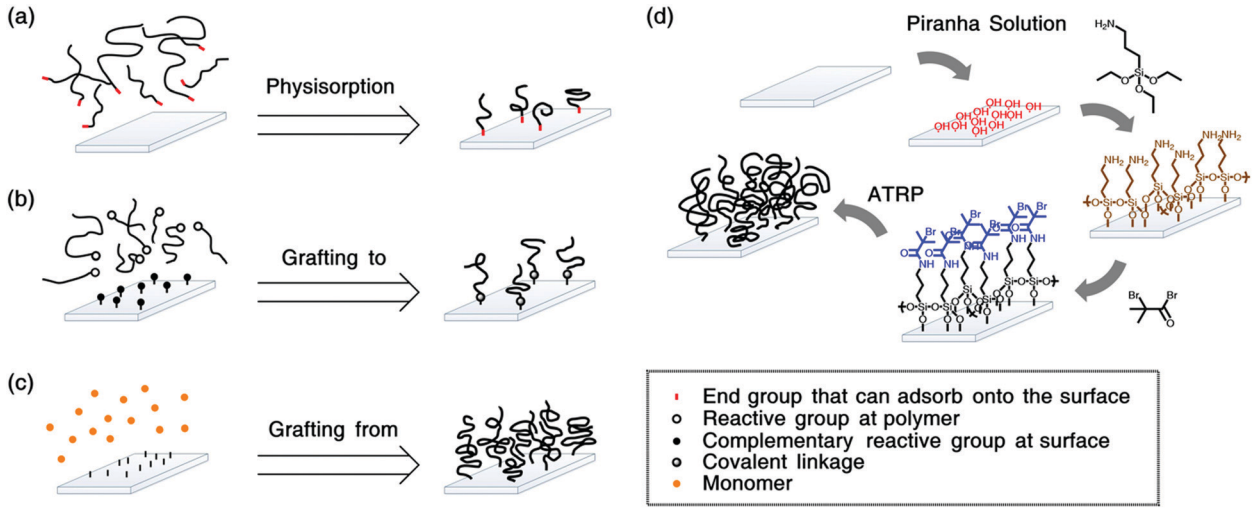

Fig. 1 Synthesis techniques for polymer brushes (a) physisorption of polymers by surface attractive groups or blocks, (b) grafting of polymers with reactive groups to substrates with complementary reactive groups, (c) grafting of polymers from the substrate. In (d) a typical "grafting from" synthesis scheme is shown, where first silicon wafers are activated *via* immersion in piranha solution. Next, they are functionalised with aminoalkylsilanes to which the initiators (here 2-bromo-2-methylpropionyl bromide (BIBB)) are coupled. Finally, the brushes are polymerized from the initiators, *e.g. via* atom transfer radical polymerization (ATRP). These brushes are typically not stable.

times the radius of gyration, the polymers do not interact and form mushrooms in good solvents. When these low-density polymers are in a poor solvent and/or strongly interacting with the substrate, pancakes instead of mushrooms are formed.[40] Only when the grafting density is sufficiently high and the distances between anchors is much smaller than the radius of gyration,[2] polymer brushes are formed. At these grafting densities, the chains interact and stretch away from the substrate.[41] Besides the grafting density, the degree of stretching is also determined by the solvent quality. In poor solvents, the polymers form a dense film on the substrate, while in good solvents, the polymers absorb the solvent and stretch more strongly away from the substrate.[42,43] When polymers are in the brush regime, their change in swelling in response to adjustments in the solvent environments acts in the direction perpendicular to the grafting substrate alone. This enhances their responsivity and can be utilized in the development of switchable or adaptive coatings.[44,45] Those high-density stretched surface grafts are the focus material of this review.

For the preparation of polymer grafted surfaces, three strategies can be followed[46] (see Fig. 1). Polymers can be physisorbed to substrates *e.g.*, *via* diblock copolymers, where the shorter block has an affinity for the substrate (see Fig. 1a). This method is straightforward to apply. However, it is difficult to obtain sufficiently high grafting densities due to steric hindrance. Therefore, often mushrooms, or pancakes are formed instead of brushes. Moreover, the surface bonds are relatively weak such that the polymers can easily detach by thermal of solvation effects.[47] Polymers that are covalently bonded to the substrate will be more stable. This can be achieved by "grafting to",[48] as depicted in Fig. 1b. In this method, reactive end-groups on the polymers can bond *via* complementary reactive groups on the substrate. Even though these coatings are more stable, it remains challenging to obtain

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grafting densities that are high enough to reach the brush regime.

To obtain polymer brushes with high grafting densities, the "grafting from" synthesis-method is typically employed.[49,50] (see Fig. 1c) In this method, the macromolecules are polymerized from initiators on the substrate. For these surface-initiated (SI) approaches, controlled radical polymerization techniques, such as atom transfer radical polymerization (ATRP),[51–53] nitroxide mediated polymerization (NMP)[54] or reversible addition–fragmentation chain transfer (RAFT),[55–57] are utilized to ensure a narrow dispersity of the polymers. Fig. 1d shows a typical synthesis procedure to grow brushes *via* SI-ATRP.

Polymer brushes are typically grown from well-defined surfaces such as silicon[58–60] or gold.[61–63] For silicon wafers, initiator coupling is often achieved by silane chemistry,[64,65] while gold surfaces are frequently decorated with initiators using disulphides or thiols.[66–68] We note that the surface initiated synthesis is not limited to these substrates and it has been shown that brushes can be grown from more complex surfaces, such as cellulose nanocrystals[69] or porous membranes,[70] carbon nanotubes,[71] mica,[72,73] silk fibrion,[74] or cotton fibres.[75]

Most applications of polymer brushes rely on the coatings being stable for long times. However, it was realized early on that the brushes can degrade or degraft in time.[76,77] In Fig. 2, two examples of degrafted brushes are given. There can be different reasons for brush deterioration. For example, the polymers themselves can oxidize and degrade. This has been observed for *e.g.* poly(ethylene glycol) polymers,[78] poly(lactic acid) brushes[79] and poly(phosphoester)s[80] and it can be prevented by choosing more stable monomers/polymers[81] in the preparation of the brushes.[82] Yet, in most dense brush systems, the polymers are reported to degraft at their substrate anchors, where, depending on the type of anchor, bonds can be weaker[83] and tension is the highest.[84] This degrafting can be intentional[85–87] (*e.g.* to characterize the molecular weight of the polymers) or unintentional. In the following, we focus on the latter.

In this review, we provide an overview of synthetic strategies that are aimed at anchoring polymer brushes more strongly to the substrate. Though strategies for stable brushes have been developed for "grafting to" as well,[88,89] we will focus here on brushes prepared by "grafting from", because they lead typically to high grafting density brushes. We start by discussing the proposed mechanisms for degrafting of polymer brushes and describe the different bonds that can break depending on the substrate and the type of substrate anchor. Next, we will provide an overview of the different synthetic strategies that have been developed to reduce the probability of degrafting such that the brushes will be stable for longer times. We finalize this review with an outlook and open questions and challenges in the field.

2. Proposed mechanisms for degrafting

When polymers are end-tethered to a substrate, they stretch perpendicular to the surface to form a brush. This stretching

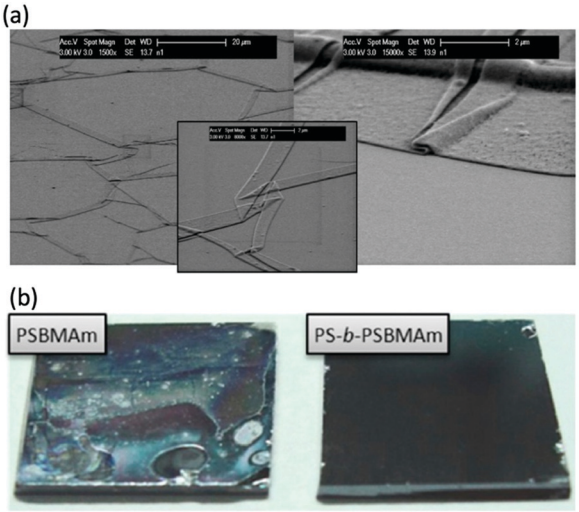

Fig. 2 (a) Scanning electron microscopy pictures displaying the detachment of poly(poly(ethylene glycol) methacrylate) (PPEGMA) brushes grafted from SiOx substrates using silane chemistry, after 7 days of immersion in a cell culture medium at 37 °C (reprinted with permission from ref. 76. Copyright 2008 American Chemical Society), (b) photos displaying the detachment of poly(sulfobetaine methacrylamide) (SBMAm) brushes grafted from silicon wafers *via* silane linkers (left), after immersion for 3 months in seawater and the prevention of this detachment by utilisation of diblock copolymer brushes (see also Section 3.2) (reprinted with permission from ref. 141. Copyright 2013 American Chemical Society).

results in an enhanced tension, which is highest at the anchor-points to the substrate. The tension is enhanced when polymers stretch more. Therefore, it increases for higher grafting densities or when the brushes are swollen in good solvents. Taking these effects into account, the tension at the anchors can be estimated to be around 1–10 pN.[84] These forces are too low to break covalent bonds. To break C–C bonds, forces on the order of nN are needed, which can only be achieved by dendrimer structures[84] or bottlebrushes on substrates.[90] However, the lower tensions in brushes can still facilitate degrafting, since they can "mechanochemically" reduce activation energies,[91] in particular at the weaker or hydrolysis sensitive surface bonds.[83]

Experimental observations are consistent with the hypothesis that polymer brushes detach by tension-enhanced breakage of the surface bonds. Wang and Klok have shown in a recent publication[92] that the degrafting rate for brushes increases upon increasing the solvent quality and thus swelling of these brushes in different (water-miscible) organic solvents, which shows that a higher tension results in faster degrafting, in agreement with earlier observations.[93] Another confirmation that tension enhances the degrafting has been provided by Chen *et al.*[94] These authors observed that the detachment rate of polymers in nanopatterned brushes decreased for decreasing pattern sizes. The reason for this is that in smaller patches the polymers are stretched less, because they can relax in the lateral directions.[94] All these results are also consistent with the general observation that the degrafting rate increases with increasing grafting density and, thus, tension at the anchors.[95–97]

Moreover, it is often observed that degrafting proceeds until a finite film thickness is reached,[98,99] which indicates that the mechanochemical effect reduces when the tension reduces, until it is too low to facilitate degrafting over the timescale of the experiment.

To ensure that polymers indeed detach and not degrade *via* side chain or backbone breakage, Du *et al.*[100] used X-ray photoelectron spectroscopy (XPS) to show that the composition of the material on the substrate does not change before and after degrafting. Moreover, they checked with proton nuclear magnetic resonance (H-NMR) and gel permeation chromatography (GPC) that the polymers in bulk do not change in chemical composition or molecular weight.[100] This has been confirmed by Wang and Klok,[92] who analyzed the molecular weight of polymers that are intentionally cleaved off at the start of the experiment and after partial degrafting. They observed a small decrease in the molecular weight ($\sim$6%), which indicates that longer polymers detach first,[95] but that they stay intact. In addition, Wang and Klok showed in the same article that their hydrophobic brushes did not degraft when being swollen in organic solvents alone. Their polymers only detach when sufficient water is present. These results are a strong indication that the brushes break at their anchors because the brushes were grafted from hydrolysis-sensitive anchors and water is needed for the hydrolysis reaction to occur (see also Section 2.1).

Degrafting of brushes is mainly observed in liquid media. Yet, it was recently shown that brushes[101] or even initiator layers[102] can degraft in air as well. When brushes are exposed to vapors that are good solvents, they swell and absorb the vapor.[103–106] Vapor-solvated swelling ratios are smaller than the swelling ratios in liquid.[60] Nevertheless, hydrophilic brushes such as poly(3-sulfopropyl methacrylate potassium) (PSPMA) and poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) can absorb sufficient amounts of water vapor from the air to allow for the detachment of $\sim$10–50% of the polymers over 8 weeks.[101]

In the discussions above, it has become clear that the experimental evidence supports the hypothesis that brushes degraft by tension-enhanced breakage of surface bonds. What surface bonds are broken exactly, depends on the grafting substrate and the type of anchor that is used. Since brushes are grafted most often from silicon wafers, we will discuss potential mechanisms for debonding on those substrates first.

2.1 Hydrolysis of siloxane, amide or ester bonds

For brushes that are grafted from silicon wafers, the initiators are often coupled to the substrates *via* silanes.[49] This can be achieved *via* a single-step or a two-step process. Fig. 1d gives an example of a two-step process. There, first, (3-aminopropyl) triethoxysilane (APTES) is coupled to hydroxyl groups on the substrate. Next, the initiator 2-bromo-2-methylpropionyl bromide (BIBB) is linked to the silanes, from where the brushes are polymerized.[107,108] Brushes grown from these anchors are well known to degraft,[101,109,110] even though they are more stable than monosilanes[97,111,112] and can be utilized with minimal degrafting for over an hour.[113] The higher stability of APTES and other trifunctional silanes can be attributed to their ability to potentially form three bonds with the substrate and/or neighbouring silanes.[65,114] In addition, it has been observed that the silane stability depends on the pre-treatment of the SiO_2 as well as temperature.[115] Nevertheless, the anchors can hydrolyse *via* their siloxane or amide bonds. Thus, eventually, they will degraft.

Polymer brushes grafted from silicon wafers have been proposed to detach *via* hydrolysis of three bonds:[98] siloxane, amide and ester bonds. The hydrolysis of siloxanes has an activation energy of approximately 100 kJ mol^{-1} [116–118] and is commonly observed.[119] However, amide and ester bonds are not expected to be cleaved at neutral pH. Nevertheless, some polymers (such as poly(acrylic acid) (PAA)[120]) might change the local acidity or basicity in the brush, such that cleavage can occur. Moreover, it has been suggested that tension can lower the activation barrier for hydrolysis and thereby allow for amide and ester bond breakage at neutral pH.[121] Indeed, Galvin *et al.* have shown that brushes grown from surface anchors that contain amide groups detach faster than brushes grafted from anchors that are similar, but have ester instead of amide groups.[96] Moreover, Ataman and Klok observed that amide- or ester-bearing brush-anchors without siloxane bonds degraft at rates that are comparable to anchors with siloxane bonds.[98] This indicates that siloxanes, amides and esters can all contribute to the degrafting process.

2.2 Cleavage of Au–S

Gold is another substrate material from which brushes are commonly grown, since it allows for surface plasmon resonance measurements[122] or to exploit the electro-responsiveness of charged polyelectrolyte brushes.[123] On such Au substrates, the initiators are often coupled *via* thiols or disulphides. However, the Au–S binding energy is only 120 kJ mol^{-1},[124,125] which makes the bond thermally unstable for temperatures above 60 °C.[126] This troubled early synthesis of brushes on gold, in particular for polymerization temperatures above room temperature.[127] Yet, with ATRP at room temperature[61] or UV photo-polymerizations,[128] it is possible to grow brushes from gold. Nevertheless, even when the grafting of brushes from gold or other metals using thiol linkers is successful, the brush polymers can degraft when immersed in good solvents.[129–131] For example, Zhang *et al.*[129] observed the degrafting rate of carboxylated poly(oligo(ethylene glycol) methacrylate-*random*-2-hydroxyethylmethacrylate) (carboxylated poly(OEGMA-*r*-HEMA)) is mainly determined by the swelling ratio, which has been attributed to the increased tension at the surface bonds for more highly swollen brushes.

In summary, brushes can degraft from different commonly employed substrates (*e.g.* SiOx, gold or other metals). Therefore, multiple strategies have been developed to prevent this degrafting. In the following section, we will provide an overview of these strategies and discuss the advantages and disadvantages of the proposed synthesis routes.

3. Synthetic strategies against degrafting

To counteract the degrafting of polymer brushes, many different synthesis routes have been developed. We have grouped

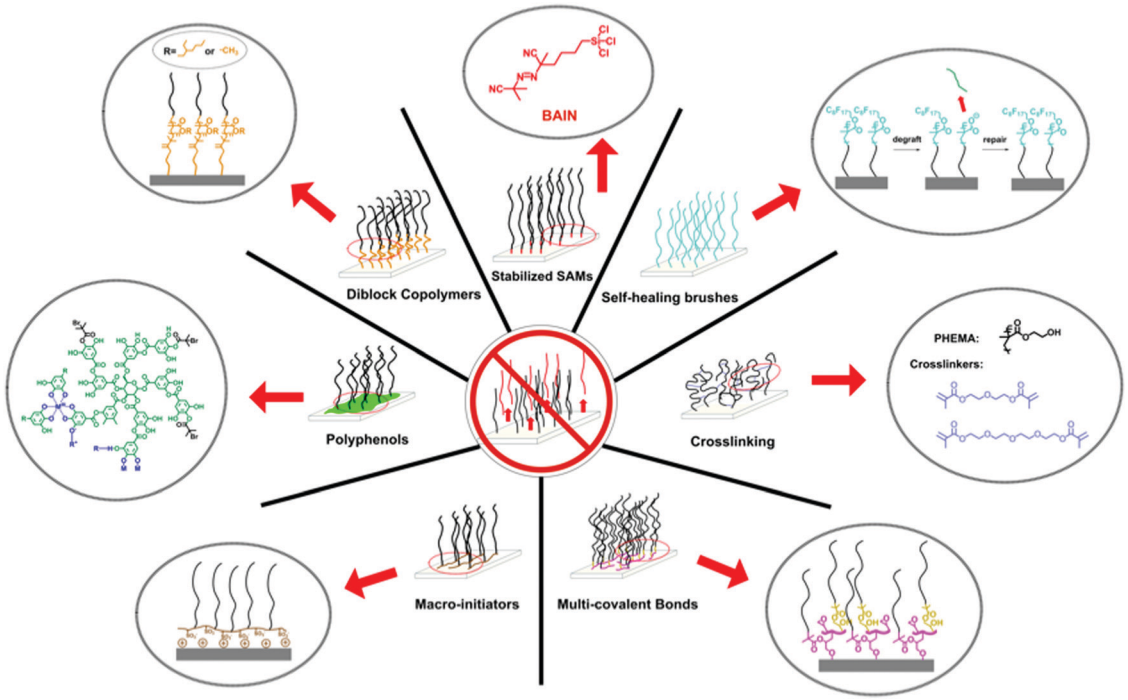

Fig. 3 Overview of the different synthetic strategies that have been developed to prepare long-term stable polymer brushes and that are being reviewed in this article.

these routes into seven strategies (see Fig. 3). Each of these strategies has different advantages and disadvantages, which we will discuss in more detail below, and it will depend on the application, substrate material and synthesis skills of the user, which strategy is the best solution.

3.1 Stabilized SAMs

Because the hydrolysis of siloxanes is one of the main mechanisms for degrafting, linker molecules have been designed that do not form Si–O–Si bonds. For example, Borozenko *et al.*[132] showed that poly(acrylic acid) (PAA) brushes grafted from phosphonic acid-based initiators resist degrafting more than brushes grown from organosiloxanes. Using density functional theory (DFT), they show that the enhanced stability is a result of the surface bond strength for organophosphonic acid initiators in water being 120 kJ mol^{-1} higher than for organosiloxanes.[132] Also Nguyen *et al.*[133] designed a method to attach initiators without having to form hydrolyzable Si–O–C and Si–O–Si bonds. They utilized a three-step reaction to couple initiators that are anchored by stable Si–C bonds and showed that low-fouling hydrophilic zwitterionic brushes grafted from these initiators are stable for >1 week.

Besides circumventing siloxane bonds, the long-term stability of brushes can be improved by preventing the usage of ester-bonds as well. Bain *et al.* synthesized ester-free initiator molecules called BAIN (named after the first author). They showed that quaternized poly(2-(dimethylamino)ethyl methacrylate) (qPDMAEMA) brushes degraft by less than 10% over 5 days (see Fig. 4a).[134] For comparison (Fig. 4b), when the same brushes are grafted from [11-(2-bromo-2-methyl)propionyloxy]undecyltrichlorosilane (BMPUS),

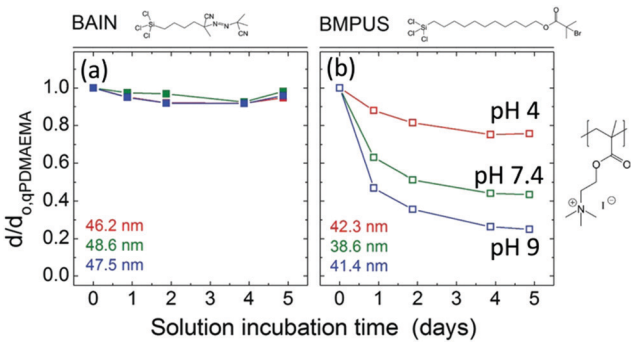

Fig. 4 The brush height d normalised by the initial brush height d0,qPDMAEMA for brushes (a) grafted from ester-free BAIN initiator molecules and (b) BMPUS initiator molecules. The heights given in colour in the bottom left of the graphs are the initial heights of the brushes in the experiments given in the respective colour (adapted with permission from ref. 134. Copyright 2012 American Chemical Society).

which is an initiator with an ester bond, the brushes degraft by up to 80% over 5 days in solution (pH = 9).

For gold substrates, synthetic routes that result in more stable polymer brushes have been developed as well. Park *et al.*[135] showed that brushes can be grafted from gold at elevated temperatures (120 °C) using bromoisobutyrate-terminated alkanethiols, 16-(3,5-bis(mercaptomethyl)phenoxy)hexadecyl 2-bromo-2-methylpropanoate (BMTBM) as initiators. The enhanced stability of these molecules was attributed to the chelate effect: the molecule has an aromatic ring with two thiol groups that can chelate readily to the gold substrate. An alternative, more stable synthesis route is the silanisation of thiol based initiators,[136] which

links the initiators to each other. This allows for stable grafting of the brushes from the initiators. Moreover, it makes the grafted brushes stable for 3 h at temperature of 150 °C. However, due to the presence of siloxane and amide bonds, these brushes can still degraft. A more stable route for gold (or metal) attachment can be achieved *via* aryl diazonium salts.[137,138] For example, Matrab *et al.* electrografted initiators based on aryl diazonium salts.[137] Optimization of this process by Iruthayaraj *et al.*,[138] resulted in stable high density brushes *via* covalently bonded initiators without any hydrolyzable bonds.

The advantage of the linker molecules described above is that they form dense self-assembled monolayers (SAMs), such that the initiator density at the substrate is high as well. Therefore, polymer brushes can be grown with grafting densities that are comparable to the grafting densities obtained with the more common silanes used for silicon and mica or thiols used for gold. A disadvantage of most of the described linkers is that the molecules are not commercially available, and the synthesis involves several steps. This makes it more challenging to employ these techniques on large scales. Moreover, the proposed initiator linkers might be less effective for initiation of the polymerization.[49,51]

3.2 Diblock copolymers

Several groups have proposed diblock copolymers as promising systems for enhancing the stability of polymer brushes.[139–143] They are prepared in a two-step SI-ATRP reaction. First, hydrophobic anchor blocks are grafted from the surface. Their function is to protect the sensitive bonds near the surface. Next, the second block is polymerized from the chain ends of the first block. This block will be hydrophilic. When immersed in water, the diblock copolymer brushes will consist of a dense, collapsed layer near the substrate (anchor blocks) and a swollen brush on top of them (hydrophilic block, see also Fig. 3).

An overview of different proposed diblock copolymer brush systems and their performance is given in Table 1. From these performances several conclusions can be drawn. First of all, more hydrophobic anchor blocks appear to result in more stable brushes. Quintana *et al.*[141] compared poly(styrene) (PS) and poly(methyl methacrylate) (PMMA) anchor blocks and found that the hydrophilic poly(sulfobetaine methacrylamide) (PSBMAm) brushes grafted from the more hydrophobic PS are more stable. However, not only the hydrophobicity is important to consider. Divandari *et al.*[142] observed that PMMA anchors are more stable than poly(lauryl methacrylate) (PLMA) anchors, even though PLMA is more hydrophobic. They attribute this to the PMMA being glassy, while PLMA has a glass transition temperature below the experimental temperature of 37 °C. Consequently, PMMA will be mechanically more stable than PLMA.

Besides the hydrophobicity and the glassiness of the anchor blocks, also the thickness of these blocks is important. Li *et al.* observed that the height of PMMA-*b*-PAA polymer brushes with a PMMA anchor thickness of 11 nm decreased to 88%, while the same brushes with a PMMA anchor height of 2.8 nm decreased to 78% (see also Table 1). From all these observations we can conclude that the anchor block of diblock copolymer brushes needs to be hydrophobic, glassy and of sufficient thickness (>20 nm) to prepare long-term stable polymer brushes.

A major advantage of diblock copolymers as a synthetic strategy for stable brushes is that truly long-term stability can be achieved (even after several months of immersion in seawater[141]). Nevertheless, there are several disadvantages as well. The grafting density of the second block is typically lower than the first block due to termination of the polymerization during the grafting of the anchor block, and limited availability of chain ends during second polymerization. Moreover, the synthesis relies on multiple complex steps, which limits its applicability.

3.3 Bio-inspired polyphenols

Since the first report of mussel-inspired, strongly and (almost) universally adhering polydopamine films,[144] these coatings have been utilized as an initiator primer for surface initiated polymerizations as well.[145–147] Brushes grafted from these mussel-adhesive inspired films on noble metals, metal oxides, and inert polymers have been reported to be stable against degrafting.[148,149] For example, Kuang *et al.* synthesized bifunctional tripeptide bromide (BrYKY),[148] which bears both a initiating and surface attachment

Table 1 Overview of the composition, testing conditions (medium, pH and temperature T) and stability performance of different diblock copolymer brushes comosed of an anchor block of thickness d_a and a brush block of thickness d_b. The following abbreviations are used poly(methyl methacrylate) (PMMA), poly(2-ethylhexyl methacrylate) (PEHMA), poly(methacrylic acid) (PMAA), poly(styrene) (PS), poly(sulfobetaine methacrylamide) (PSBMAm), poly(oligoethylene glycol methacrylate) (POEGMA), poly(lauryl methacrylate) (PLMA), poly(butyl methacrylate) (PBMA), Dulbecco's modified eagle's medium (DMEM), poly(poly(ethylene glycol) methacrylate) (PPEGMA), poly(acrylic acid) (PAA) and room temperature (RT)

Anchor	d_a [nm]	Brush	d_b [nm]	medium	pH	T [°C]	Performance	Ref.
PMMA	40	PMAA	−1	NaOH solution	12	37	100% after 80 h	140
PEHMA	48	PMAA	42	NaOH solution	12	37	65% after 10 h	140
PMMA	20	PSBMAm	8	Sea water	8.2	37	0% after 4 weeks	141
PS	19	PSBMAm	9	Sea water	8.2	37	33% after 14 weeks	141
PMMA	23	POEGMA	21	DMEM solution	7.4	37	No observable changes after 7 days	142
PLMA	21	POEGMA	27	DMEM solution	7.4	37	Degrafting after 6 days	142
PBMA	27	POEGMA	36	DMEM solution	7.4	37	Degrafting after 4 days	142
PMMA	11	PAA	70	Ethanolamine solution	9	RT	88% after 120 h	143
PMMA	2.8	PAA	70	Ethanolamine solution	9	RT	78% after 120 h	143
PPEGMA	10	PAA	70	Ethanolamine solution	9	RT	77% after 120 h	143
PPEGMA	3.5	PAA	70	Ethanolamine solution	9	RT	69% after 120 h	143

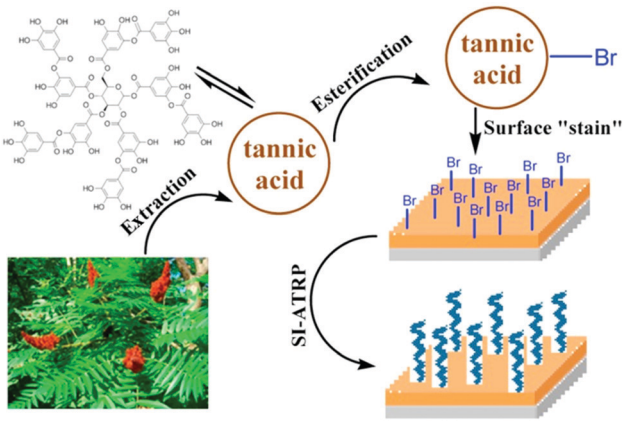

Fig. 5 Schematic representation of the synthesis of long-term stable polymer brushes from brominated, tea-stain inspired tannic acid films. Adapted with permission from ref. 151. Copyright 2015 American Chemical Society.

functionality. High-density pSBMAm brushes grafted from BrYKY kept their low-fouling performance for at least 4 months. This is much longer than observed for anchors based on SAMs of individual catechols,[150] for which the performance declined after 1 month already. This has been attributed to the multiple bonds that BrYKY can form with the substrates.

In a similar bio-inspired approach, initiator primers can be formed by tea stains.[151–153] By bromination[151,153] or direct UV activation[152] of tannic acid based anchoring layers, long term stable brushes can be prepared by consecutive surface initiated polymerization. For example, Pranantyo *et al.*[151] showed several cationic and zwitterion brushes grafted from brominated tannic acid attached to stainless steel (see Fig. 5 for the synthesis scheme) are stable against degrafting for 14 days in a stream of sea water.

The synthetic strategy based on bio-inspired polyphenols has the advantage that the initiator primers are easy to apply (*e.g.* by dip coating or drop casting). Moreover, true long term stability of several months[148] can be achieved. Nevertheless, the primer cannot be strictly universally applied. Though the polyphenol layers bind strongly to metal(-oxide) substrates[154] and carbon-based materials,[155] they not adhere well to SiO_2 substrates. In fact, this weak adherence to silicon has been utilized to prepare brush-coated polydopamine-based nanosheets.[156,157] This makes this method less suitable for several applications, for example in micro-electromechanical systems (MEMS)[158] and (nano-)photonic devices[159] where often SiOx's are the primary material.

3.4 Macro-initiators

In the descriptions of the previous sections, we stated several times that initiator molecules that have multiple bonds to the substrate exhibit an enhanced stability compared to molecules, with single surface bonds (*e.g.* in silane,[111] thiol[135] and catechol[148] binding). Macro-initiators function by the same mechanism. Macro-initiators are composed of long macromolecules with both initiating sites and moieties that can bind to the substrate.[160] This binding is often physical (electro-static). Therefore, the binding strength of a single moiety with the substrate is not strong. Yet, the total binding strength can be very strong, since it is amplified by the inherent cooperativity *via* the many binding sites between the macromolecules and the substrate.

The macro-initiators are typically bonded to the substrate *via* hydrogen bonding or electrostatic interactions. An example of the former is the binding of diazo bearing poly(ε-caprolactone)s to hydroxyl groups on silicon.[161] To exploit electrostatic interactions, cationic or anionic polyelectrolytes can be used as macroinitiators.[162,163] For example, Chen *et al.* synthesised cationic random copolymers of 2-(dimethylamino)ethyl methacrylate (DMA) and 2-hydroxy-ethyl methacrylate (HEMA), in which the hydroxy groups of the HEMA monomers were esterified using 2-bromoisobutyryl bromide to form the initiator groups and the DMA was quaternized to introduce the positive charges. These macroinitiators can be bound to negatively charged substrates such as silica.

From macro-initiators one can graft stable polymer brushes, as was shown by Rodda *et al.*[164] They grafted poly(oligo(ethylene glycol) methacrylate) (pOEGMA) brushes from poly(styrene-*co*-vinylbenzyl chloride) macroinitiators and observed that these brushes were stable for at least 24 h in cell culture media.[164] This is comparable to the performance of pOEGMA brushes grafted from silane-based initiators.[165] Nevertheless, using a different technique, the same group showed that pOEGMA brushes grafted from brominated polycaprolactone (PCL) macroinitiators resulted in them being stable for >21 days.[166] Alternatively, brushes can be grafted from crosslinked physisorbed polyvinylpyrrolidone (PVP) on the substrate. Sun *et al.* showed that PVP brushes grafted from such crosslinked PVP films are stable for 4 weeks.[167]

A major advantage of the utilization of macro-initiators is that these initiator coatings are easy to apply as a primer layer on the substrate. Nevertheless, the synthesis of the macro-initiators often involves several synthesis steps. Moreover, the initiator surface coverage is often smaller than for SAM-based initiator layers. Though higher density brushes can be obtained by layer-by-layer deposition of the anchor.[168] Nevertheless, the bonding is based on physical interactions, which can change if the environment (*e.g.* pH or salt concentration) is varied. Therefore, the brushes can degraft under unfavorable conditions.

3.5 Multi-covalent bonds

The synthetic strategy that utilizes multi covalent bonds is closely related to the macro-initiators described in Section 3.4. Yet, the strategy described here eliminates an important disadvantage of macro-initiators, which is that debonding of the physisorbed macromolecules can occur by *e.g.* pH changes. This debonding can be circumvented by covalently bonding the macromolecules to the substrate.

Multi-covalent bonding has been obtained by poly(glycidyl methacrylate) (PGMA) polymers. The epoxy groups of PGMA can react with for example hydroxyl groups on different types of substrates. Next, initiators can be attached to the PGMA, from which brushes can be grafted[109,169] (see Fig. 6a). These brushes

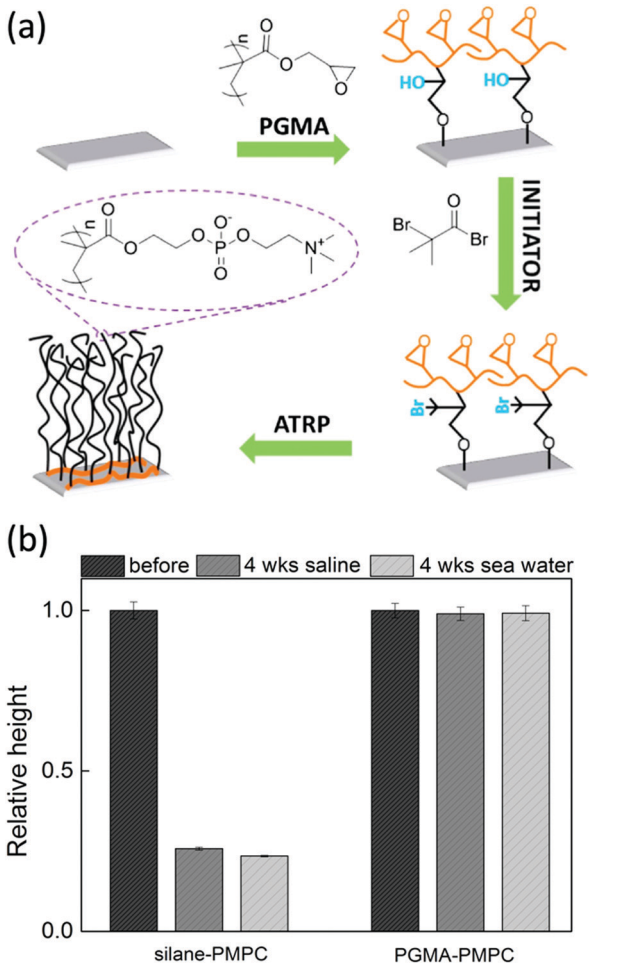

Fig. 6 (a) Synthesis scheme for the preparation of poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) brushes on silicon surfaces by grafting the brushes from initiators attached to PGMA. The PGMA is attached to the substrate *via* multiple covalent bonds (adapted from ref. 109). (b) The relative height of PMPC brushes grafted from unstable silanes (left) and from PGMA attached initiators (right) after immersion for 4 weeks in saline solution (dark gray) or artificial seawater (light gray).

are very stable, even under harsh oxidative environments.[109] The enhanced stability can be attributed to different reasons. First, the PGMA can only detach if all bonds are broken, which will slow down degrafting. Moreover, the hydrophobicity of PGMA can prevent water from reaching the hydrolysis sensitive PGMA-substrate bonds. In fact, when we make the PGMA anchor more hydrophilic by coupling polyethylenimine (PEI) before polymerization, the brushes do degraft.[170]

For example, in our research group, we have shown that poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) brushes grafted from multi-covalently bonded PGMA are stable for more than 4 weeks while being immersed in saline solution or artificial seawater. Moreover, the brushes keep their hydrophilic properties even after being kept in a highly oxidative sodium hypochlorite solution for 100 000 ppm hours.[109] In a different study, we showed that PGMA can be utilised as a stable anchor-layer to graft anti-fouling poly(3-sulfopropyl methacrylate potassium) (PSPMAK) brushes on artificial implants.[110] The brushes displayed less than 10% degrafting after being immersed in aqueous solutions for more than 32 days.

An alternative route to prepare multi-covalently bonded initiator layers was presented by Kang *et al.*[171] They prepared crosslinked P(S-*r*-GMA) anchor films to graft brushes that were stable upon repetitive washing and during multiple thermal annealing cycles. Moreover, the grafting density could be controlled by varying the GMA/S ratio.

A major advantage of this synthetic strategy is that the initiator film is strongly bonded to the substrate *via* multiple covalent bonds, giving rise to long-term stable brushes even under harsh oxidative conditions. Nevertheless, there is also a clear disadvantage: the initiator density in the film is low compared to that for SAMs. Moreover, the initiator moieties are 'hidden' under the protective PGMA film. Therefore, one typically obtains lower grafting densities of 0.1–0.2 chains per nm^2, especially for bulky monomers such as MPC and SPMAK.

3.6 Crosslinking

In parallel with the development of strong substrate anchors, researchers have designed complementary strategies to increase the stability of polymer brushes. Crosslinking of the brush can strongly enhance the long-term stability of the brushes.[76] In a recent report, Chen *et al.*[172] showed that the crosslinked edges of patterned brushes do not degraft, while the non-crosslinked centers of the patterned brushes do degraft. To effectively increase the stability of brushes, one needs to keep in mind that enough links are formed such that one is beyond the gelation threshold for crosslinked brushes.[173] Then long-term stable brushes can be formed: Wu *et al.* showed that crosslinked brushes can keep their antibacterial properties for more than 4 weeks of immersion in water.[174] Moreover, crosslinked brushes can resist high shear stresses, while maintaining their lubricating properties.[175]

An alternative method to introduce extra bonds can be achieved *via* a ladder-structure, as recently presented by the lab of Zapotoczny.[176] Słowikowska *et al.* observed that the degrafting of ladder-structured poly(3-trimethylsilyl-2-propynylmethacrylate) (PTPM) brushes in tetra-butyl-ammonium fluoride (TBAF) solution is significantly slowed down compared to the linear counter parts. While the linear brushes degraft completely in 2 h, the ladder brushes still have 33% of their brush height after 25 h.[177] The increased stability can be attributed to the additional intra- and intermolecular bridges as well as the reduced swelling.

Though the synthesis of ladder-brushes is highly specialized, a primary advantage of crosslinked brushes is that this crosslinking is often easy to achieve. Nevertheless, there are several disadvantages as well. The brushes of these alternative topologies will swell less and have different mechanical properties than traditional brushes. Moreover, the degrafting is only delayed. Since water can still reach hydrolysis-sensitive bonds, degrafting will eventually occur.[76]

3.7 Self-healing brushes

An out-of-the-box solution that does not prevent degrafting but will, nevertheless, give rise to a longer performance time of brush-based coatings, is the development of self-healing

Table 2 Overview of the advantages and disadvantages of the synthetic strategies described in this review, with SI-ATRP being surface initiated atom transfer radical polymerisation, PGMA being poly(glycerol methacrylate) and p(S-*r*-GMA) being a random copolymer of styrene and glycerol methacrylate

Strategy	Chemistry	Advantages	Disadvantages
(1) Stabilized SAMs	(a) Phosphonic acid based initiators on SiO_2[132] (b) Direct Si−C linkage on Si_xN_4[133] (c) Ester-free initiators on SiO_2[134] (d) Chelate effect on gold[135] (e) Silanisation thiols on gold[136] (f) Aryl diazonium salts on gold[137,138]	High density brushes	Multiple-step synthesis
(2) Diblock copolymers	Consecetive polymerizations *via* SI-ATRP[140–143]	Strongly enhanced stability (up to months)	Multiple synthesis steps and low grafting densities
(3) Polyphenols	(a) Polydopamine[148,149] (b) Tannic acid[151–153]	Synthesis is easy and long-term stability	Cannot be applied to all substrates (not for SiOx)
(4) Macro-initiators	(a) Brominated polycaprolactone[166] (b) Polyvinylpyrrolidone[167] (c) Multi-layer bonding for high grafting density[168]	Synthesis is easy	Often low grafting density and not stable under all solvent conditions
(5) Multi-covalent bonds	(a) PGMA[109,110] (b) p(S-*r*-GMA)[171]	Synthesis is easy and long-term stability even under harsh conditions	Low grafting density, especially for bulky monomers
(6) Cross-linking	(a) Random crosslinking[76,174] (b) Ladder structure[177]	Synthesis is easy (crosslinking)	Brush characteristics can disappear
(7) Self-healing	3D grafted brushes[178,179]	Possibility for regeneration	Complex synthesis, limited self-healing events

brushes. Instead of initiator-engineering or crosslinking, as described in the previous strategies, the polymer of the brushes are now replenished *e.g. via* 3D grafting or surface re-organisation.[178] This brings the advantage of regeneration of the coating. Kuroki *et al.* designed polymer networks in which polymers were grafted both at the surface of the network as inside the network material.[179] After the surface polymers had been detached, polymers in the bulk network can be brought to the surface. With this network the authors could achieve that the longevity of the antifouling behavior of these 3D grafted brushes was 4 times as long as for 2D brushes.

While improved stability has been observed for these self-healing brushes, there are several disadvantages to this technique. The synthesis procedures for the routes developed so far are complex. Moreover, the replenishing of the coating is limited and are after a few healing cycles the healing process no longer works.

The different synthetic strategies discussed above (and summarized in Fig. 3) each have specific advantages and disadvantages. We summarize these advantages and disadvantages in Table 2. Which synthetic strategy is the best for the preparation of long-term stable polymer, depends on the demands on the coating by the application as well as the substrate materials. With the overview provided in the text and Table 2, the readers can make a more informed decision on the best solution for their specific application.

4. Outlook and open questions in the field

Though many synthetic strategies have been developed, there are still open questions that need answering. As is clear from the overview provided in Table 2, the perfect synthetic strategy to prepare long-term stable brushes does not yet exist. In particular for SiOx substrates, most strategies (*e.g.* diblock copolymers, macro-initiators and multi covalent bonds) result in brushes with lower grafting densities than can be obtained *via* SAM-based initiators. How to obtain high grafting density, stable brushes, is currently carefully examined. Similar to layer-by-layer macro-initiators,[168] layer-by-layer multi-covalent bonds could be prepared, which might result in higher grafting densities. Additionally, the anchors could be functionalized with groups that allow for a high density initiator coupling (such as tris(hydroxymethyl)aminomethane).

Additionally, to translate research on polymer brushes to applications, the synthesis route for grafting brushes from substrates needs to be simplified. Recently, several synthesis techniques have been designed that allow grafting under ambient conditions, for example by large scale Cu^0-mediated surface-initiated ATRP,[180] filter paper assisted Cu^0-mediated surface-initiated controlled polymerizations[181] or oxygen tolerant photoinduced electron transfer (PET) controlled polymerization techniques.[57,182] This will make it possible to scale up the synthesis of these brushes. Nevertheless, the synthesis for initiator primer films that give rise to long-term stable brushes still must be scaled up.

How to prepare large scale initiator primer layers is not yet widely explored. Nevertheless, the first techniques have been reported.[21,183] For example, Sato *et al.* reported on the large-scale ($\sim$40 m^2) production of initiator layers by spin-, wire-bar-, or roll-to-roll-coating of a simple sol–gel solution of (*p*-chloromethyl)phenyl trimethoxysilane (CMPTMS) and tetraethoxysilane (TEOS)[183] (see also Fig. 7). Developing routes like this will be key in the translation of polymer brush research to the large-scale application of these coatings and they need to be developed for the synthetic strategies reviewed in this article as well.

Finally, we would like to discuss the relevance of the different synthetic strategies reviewed in this article for

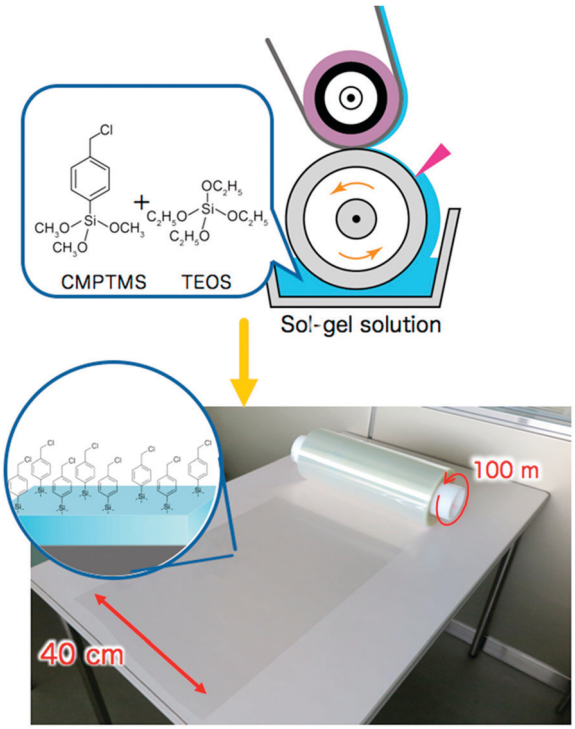

Fig. 7 Large-scale production of initiator layers by casting of a sol–gel solution of (*p*-chloromethyl)phenyltrimethoxysilane (CMPTMS) and tetraethoxysilane (TEOS), which will allow for scale up in polymer brush synthesis. Adapted with permission from ref. 183. Copyright 2018 American Chemical Society.

preparing patterned brushes. Recently, there has been a renewed interest in such patterned brushes[50] because they allow for more precise control of for example adhesion[184] and membrane transport.[185] Patterned brushes can be prepared by micro-contact[127] or inkjet printing[186] of thiols or silanes. Alternatively, photo-lithography can employed to spatially control brush growth.[187–189] However, when anchors are utilized that easily degraft, the patterned brushes will also degraft. Several strategies presented in this article allow for printing stable surface anchors. Macro-initiators,[190] anchors based on multicovalent bonding and polyphenol-based anchors, can be printed straightforwardly, since they do not immediately wet the substrate and, therefore, these strategies are recommended for preparing patterned brushes by printing. Brushes prepared by photo-lithography can utilize all presented strategies.

5. Summary

In this review article, we have presented an overview of proposed mechanisms and causes for the deterioration and degrafting of polymer brushes. Moreover, we have reviewed the status on synthetic strategies that have been developed to prevent degrafting and we identified open questions in the field. We hope that with this review we will help the reader in making an informed decision on the best strategy in synthesizing more stable polymer brushes.

Author contributions

Zhichao Ding: data curation, investigation, resources, writing – original draft. Changyou Chen: investigation, visualisation, writing – original draft. Yunlong Yu: conceptualization, funding acquisition, project administration, supervision, writing – original draft. Sissi de Beer: conceptualization, formal analysis, visualization, writing – review and editing.

Conflicts of interest

There are no conflicts to declare.

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