

# Light induced *grafting-from* strategies as powerful tool for surface modification

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**Abstract.** Chemical-induced grafting processes can be performed either by a *grafting-to* method, where preformed polymer chains are grafted on the surface previously activated, or alternatively, the polymer chains can be grown from the surface via a *grafting-from* method. The last one can be considered a bottom-up approach in which polymers are generated directly on the surface starting from their precursors. As a preliminary process, the substrate is functionalized with specific groups that can initiate a polymerization reaction. Although surface-initiated polymerizations are conventionally induced by a thermal initiator or directly by radicals formed by high energy treatment of the surface, they can be triggered by light. In this regard, light-induced grafting reactions have recently found increasing interest. With this review, by placing emphasis on the initiating system, we aim to show the significant feasibility of *photografting-from* method to properly functionalize any type of surface.

**Keywords:** *molecular engineering, grafting process, photochemistry, surface properties, photoinitiators*

## 1. Introduction

Surface modification and functionalization play an important role in many applications with enormous interests both in the academia as well as in industrial sectors [1–3]. Its significance is related to the possibility to control wettability, to improve strength in composite materials, to induced antifouling surface properties or to minimize protein absorption for medical and microfluidic analytical devices.

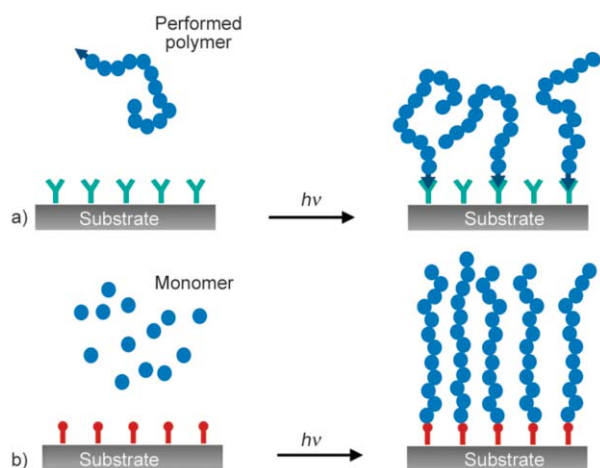
The surface modification can be either obtained via a physical or a chemical modification. While physical adsorption of polymers on a substrate is the simplest way of surface modification, it leads to modified surfaces which are often thermally unstable, unable to withstand high shear forces, and easily displaceable by chemicals or proteins and cells. On the other hand, chemical modifications give rise to the formation of stable systems characterized by a chemical bond among the surface and the polymer grafted.

Chemically induced grafting processes can be performed either by a *grafting-to* method (schematized in Figure 1a) where preformed polymer chains are grafted on the surface activated previously. Alternatively, the polymer chains can be grown from the surface via a *grafting-from* method Schematized in Figure 1b) also known as *surface-initiated polymerization*.

Among the two different strategies, the *grafting-from* methods are preferred since it is possible to achieve higher grafting density and film thickness. In fact, *grafting-to* methods show limitations due to steric hindrance between polymeric chains, which makes it difficult to tether chain ends at short intermolecular distances.

On the other hand, *grafting-from* methods can be considered as a bottom-up approach. Indeed, polymers are generated directly on the surface starting from their precursors. As a preliminary process the

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**Figure 1.** Scheme of the *grafting-to* method (a) or *grafting-from* (b) method of surface functionalization.

substrate is functionalized with specific groups that are able to initiate a polymerization reaction.

There are many reports in literature related to the surface-initiated polymerization, where a wide variety of polymerization processes are available for the *grafting-from* approach [4] including, for example, ring-opening polymerization (ROP), ring-opening metathesis polymerization (ROMP) [5] or radical polymerization. The latter may be further tuned by using one of the well-established techniques for controlled polymerization, such as atom transfer radical polymerization (ATRP), [6] nitroxide mediated radical polymerization (NMP), [7] or reversible addition–fragmentation chain transfer (RAFT) [8]. Surface-initiated controlled radical polymerization (SI-CRP), allows for precise control over polymer architecture, composition and molecular weight. Because of its versatility and tolerance toward a variety of functional groups it has been widely employed as a synthetic technique to prepare polymer brushes [9]. While the polymerization can be initiated by a thermal initiator or directly by radicals formed by high energy treatment of the surface, light induced triggering of the grafting reaction has recently found increasing interest [10]. The photoinduced method is energy efficient since heat is not required and gives the possibility of a fully spatio-temporal control of the grafting process, allowing an easy access to structured surfaces.

Comprehensive reviews which also included light-induced *grafting-from* methods have already been reported [11–15]. Nevertheless, in this review we collect the most recent progress in this field with emphasis on the initiating systems, reporting as well methods for controlled photografting as well as the

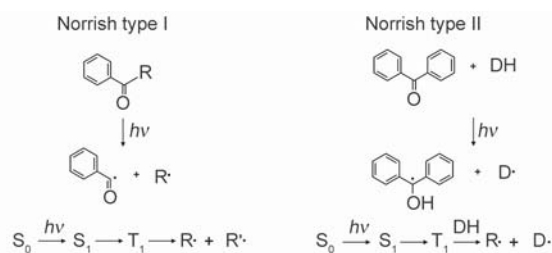
self-initiating photografting. The aim of this review is to provide the tools to properly conduct photografting modifications by selecting the most suitable initiating system from state-of-the-art scientific contributions.

## 2. Photografting initiating systems

Photografting processes exhibit important advantages with respect to thermal ones, such as: fast reaction rate, low processing cost, easy exploitation of industrialization and the possibility to spatially control the grafted chains.

The pioneering work on grafting polymerization initiated by UV light was published in the 1950s by Oster and Shibata [16] and from different authors in the late 1990s [17, 18].

Generally speaking, photoinduced polymerizations proceed by a chain reaction mechanism involving the propagation of an active center by the interaction with a monomer. The active center can be a radical, a cation or more rarely an anion. The photogenerated active species is the ‘true’ initiator that is able to initiate the polymerization of a reactive monomer, usually by addition to a multiple bond or by a ring-opening process. Usually it is a radical reactive species. The photoinitiation step of a radical polymerization reaction typically requires the presence of a molecule (photoinitiator), which absorbs the exciting light and leads to radical production. Several types of initiators have been used in the last decade. The photo-physical and photochemical processes on which they are founded have been generally well established and mainly divided into two processes: *photoscission processes*, Figure 2, where an aryl-alkyl ketones produce radical according to a Norrish type I process, ( $\alpha$ -cleavage) and *hydrogen abstraction*, Figure 2, in which a ketyl type radical is generated through photoreduction of the triplet state by hydrogen donors such as tetrahydrofuran (THF), alcohols or amines.



**Figure 2.** scheme of the different mechanism of action of the radical photoinitiator: Norrish Type I (Figure 1a) and Norrish Type II (Figure 1b).

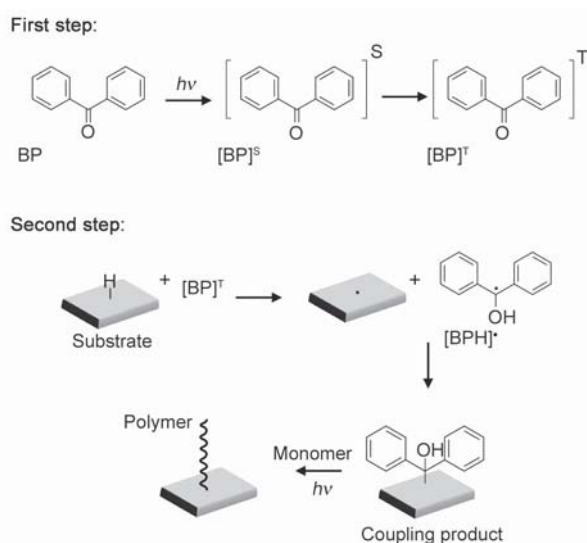
## 2.1. Norrish type II initiating systems

When using the photografting process the most used photoinitiator in order to generate radicals on the substrate surface have been the Norrish type II photoinitiator benzophenone (BP) [19, 20].

In principle, when UV irradiated, BP or BP-based molecules are excited to a singlet state and then jump to a triplet state by intersystem crossing (ISC; see Figure 3). Several studies have demonstrated that BP and its derivatives in a triplet state undergo hydrogen-abstracting reactions from substrates, consequently providing surface radicals ( $R\cdot$ ) capable of initiating surface graft polymerization. The resulting benzopinacol radicals (BP-OH $\cdot$ ) are relatively less reactive and not prone to promote free radical polymerization, but tend to participate in termination by coupling reaction.

Different substrates have been treated with BP in a first step, and subsequently photoactivated in order to promote radical chain-grow polymerization on the surface.

Some authors photografted polyacrylamide onto cotton fabrics by linking photo-active moiety benzophenone chromophoric groups. As a result, the grafting was successfully achieved, and the grafting rate increased with increasing benzophenone concentration and photo-irradiation (grafting) time. The as-grafted cotton fabrics showed significantly increased thermal stability, and also through a simple chlorination process, it obtained excellent antibacterial ability [21]. Ma *et al.* [22] proposed a two-step process to photografting polypropylene membranes: in the first



**Figure 3.** Schematization of benzophenone *grafting-from* mechanism.

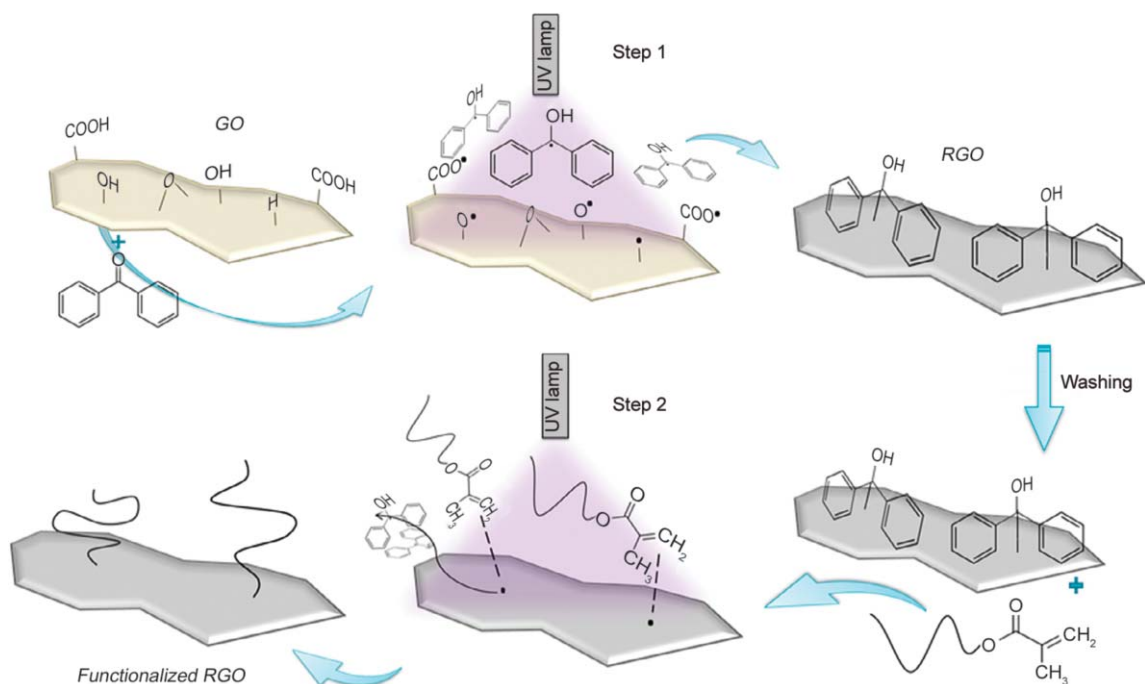
step irradiated BP is able to abstract hydrogen from PP substrate, the photogenerated radicals on the surface quickly combine with semipinacol radicals. In the second step, the monomer solution is added to the active substrate and the surface initiators initiate the graft polymerization under UV irradiation.

Roppolo *et al.* [23] followed a similar concept to photografting graphene oxide (GO) surface. The process is schematized in Figure 4. As previously discussed, by dispersing GO in the presence of BP, under irradiation the semipinacol radical are able to recombine with remaining radicals on the GO sheets creating a covalent bond. In the second step, during UV-irradiation, a homolytical break the bond between the semipinacol group and the GO surface is induced, generating an initiating point on the GO surface, so a radical chain grown polymerization is promoted in the presence of a suitable monomer.

Luan *et al.* [24] modified the surface of biomedical elastomers poly(styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene) (SEBS). Oxygen plasma process was used as pre-treatment in order to form polar onto the surface of SEBS film. This treatment improved the wetting properties of both hydrophilic NVP monomer and ethanol solution of BP initiator on the plasma-treated substrate, thus facilitating the uniform distribution of grafted chains on the surface. In the UV-induced graft polymerization process, SEBS films in BP solution were exposed to UV irradiation which caused BP initiator abstracted hydrogen from the SEBS backbones to form surface free radicals, and further initiated the surface graft polymerization of *N*-vinyl pyrrolidone (NVP) monomer. After the surface photografting with NVP, the water contact angle decreased to about 40° and protein adsorption and platelet adhesion were significantly inhibited.

Sugiura *et al.* [25] reported that the surface of polydimethylsiloxane (PDMS) can be micropatterned with poly(ethylene glycol) (PEGDA) in one step photografting process by using a reaction mixture of monomer and BP. The PEGDA-modified PDMS surface exhibited stable hydrophilicity after more than two months storage in air. Additional, the micropatterned surface showed the ability to generate micropatterned protein adsorption and cell adhesion thanks the poly(ethylene glycol) which has low protein adsorption and low cell attachment.

Schneider *et al.* [26] accurately investigated the process parameters for the photografting of the inner channel of polydimethylsiloxane microfluidic



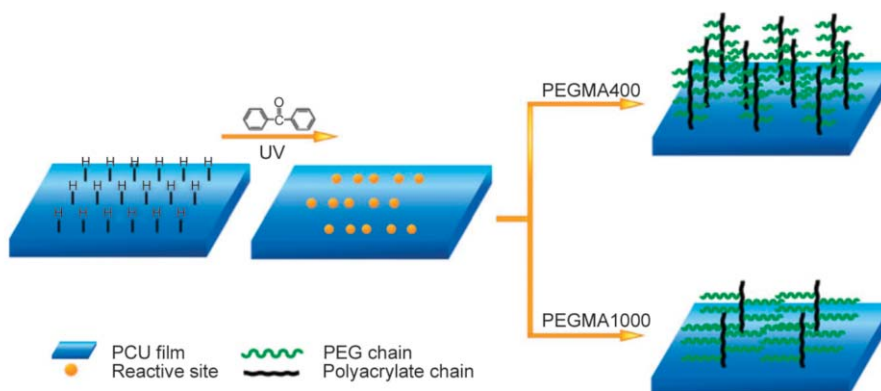
**Figure 4.** Schematic representation of the two-step photografting process of graphene oxide surface. Reproduced from ref. [23].

devices with poly(acrylic acid), PPA, even for very complex geometry. A solution of BP in acetone when applied inside the microfluidic channels diffuses into the PDMS matrix. After washing, the channels filled with acrylic acid (PA) can be exposed to UV-light to generate the photografted PPA surface.

Benzophenone as photoinitiator has also been employed in PDMS materials to photograft methacrylate monomer bearing a phosphorylcholine moiety prior photogeneration of semipinacols. It was shown that it is possible to tailor protein repellency and lubrication property by playing on the grafting density [27]. Feng *et al.* [28] anchored BP molecules onto polycarbonateurethane surfaces and, by using UV-light, induced the polymerization of poly(ethylene glycol)

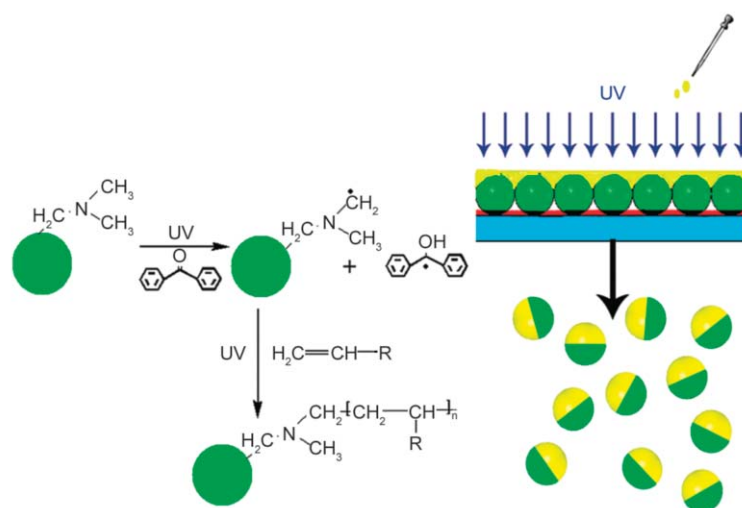
monomers with different molecular weight to improve haemocompatibility and increment hydrophilicity. They showed that monomer molecular weight affects platelet adsorption and haemocompatibility, which might be explained with an optimum balance between poly(ethylene glycol) grafting density and chain length.

It has also been recently shown that benzophenone can be used for the surface modification of cellulose with poly(ethylene glycol). Morphological analysis showed that poly(ethylene glycol) surfaces assemble in very sharp formation of very sharp nanometric architectures on the surface of cellulose [29]. Benzophenone has also been adopted in the synthesis of Janus particles (i.e. particles with topologically



**Figure 5.** Schematic illustration of poly(ethylene glycol) photografting from polycarbonateurethane films. Reproduced from ref. [28].





**Figure 6.** Preparation of Janus particles by the selective photografting of poly(styrene) particles with tertiary amine groups on surfaces by using benzophenone as photoinitiator. Reproduced from ref. [30].

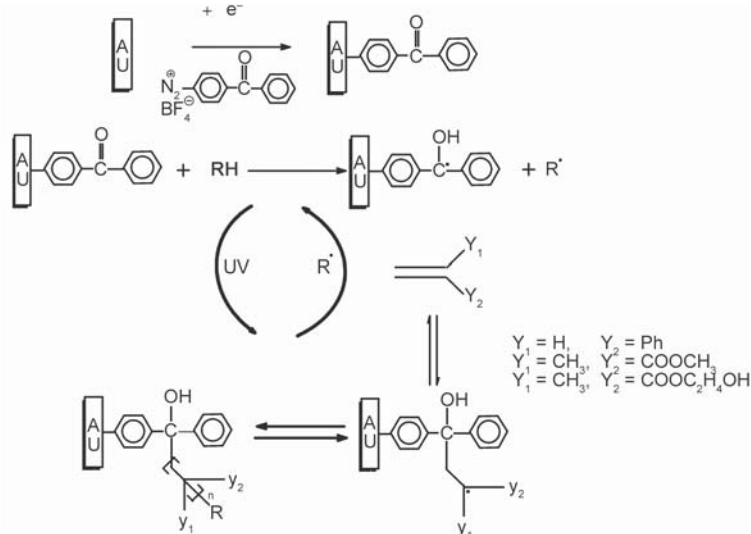
distinct domains with different chemistry) via selective photografting. In their study, poly(styrene) polymeric particles with tertiary amine groups on surfaces were immobilized on a planar substrate and treated with BP (Figure 6). Subsequently, the particles surface exposed to UV-light was photografted with poly (methacrylate) leading to the formation of particles with compartmentalized surfaces [30].

The applicability of BP photoinitiator is generally limited by the fact that the surface generation of semipinacols requires the abstraction of hydrogen and therefore this limits its use to surfaces which possess hydrogens to be abstracted. Gam-Derouich *et al.* [31] were able to extend the use of BP to metal surfaces by using a BP-derivative diazonium salt. Indeed, as illustrated in Figure 7, photoinitiator was immobilized on a gold surface via electrochemical

reduction. The immobilized photoinitiator, in along with dimethylaniline as a co-initiator, showed to be effective in the photografting of different polymer such as poly(styrene), poly(methyl methacrylate), and poly(2-hydroxyethyl methacrylate).

## 2.2. Norrish type I initiator

Derivatives of the widely used 2,2-azobis-(isobutyronitrile) (AIBN) initiator have been also adapted in surface modification via light-induced *grafting-from* [32, 33]. However, these azo initiators show a relatively low absorbency and long half-life [34] and consequently, long curing times are needed. Additionally, the photoactivation of AIBN derivatives produces two radicals with the same reactivity, only one of which is tethered to the surface. The unanchored radical diffuses into solution and initiates polymerization in the



**Figure 7.** Immobilization of benzoylphenyl photoinitiators on a gold surface via electrochemical and graft photopolymerized monomers using dimethylaniline as a co-initiator (H donor). Reproduced from ref. [31].

bulk. The so produced bulk polymer intercalates into the grafted brush and requires a time-demanding purification for complete removal.

More recently Wang *et al.* [35] proposed the synthesis of alkoxy-functionalized bis-(acylphosphane) oxides (BAPO) via a stable bis(mesityl)phosphane intermediate. The functionalized BAPO was attached on the nanocellulose particles and poly(methyl methacrylate) chains were grown by the light-triggered grafting onto the surface. In another work from the same group, a tri(methoxy)silyl-substituted BAPO derivative was attached on the cotton surface and fluorinated acrylates were photografting onto cotton fabrics [36].

Alkoxy functionalized BAPO was also proposed for the glass surface modification, obtaining a photoactive surface. By spreading the monomer on the functionalized substrate and by UV irradiation in the presence of either a partially fluorinated acrylate or a specifically synthesized polysiloxane containing polymerizable acrylate functions allowed the generation of polymer chains which grew from the surface in an efficient radical polymerization process ('*grafting-from*' procedure). Durable hydrophobic surfaces were prepared characterized by contact angles between 93 and 95° [37].

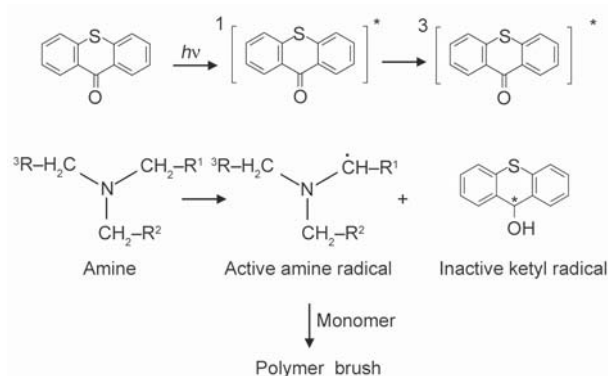
The same surface-anchored bis(acyl)phosphane oxide photoinitiator was used to fabricate silica nanoparticles homogeneously covered with poly(ethylene glycol) polymer chains or with chains of two different polymers (poly(ethylene glycol) and poly(lauryl methacrylate)) segregated in distinct domains. The authors showed how photografting strategies can be employed for the fabrication of very small Janus nanoparticles by photopatterning the surface of each single particle. The Janus-like photografting was achieved by initiating the polymerization of the hydrophilic monomer only on the free-surface of immobilized nanoparticles. In a second step, the unreacted photoinitiator functionalities were used for the photografting of the lipophilic monomer [38].

Yin and coworkers proposed another strategy involving surface-anchored dendritic thioxanthone (TX) photoinitiators. In this approach (Figure 8), in the presence of amino groups as co-initiators, light-irradiation leads to the formation of a ketyl radical from the thioxanthone and another radical coming from the hydrogen donor amine. In the presence of a suitable monomer, the polymerization is initiated by the amino radicals while the ketyl radical are generally very

less reactive because of the steric hindrance. This approach has been adopted on both planar surfaces [39] to grow poly(*N*-isopropylacrylamide) brushes and on microparticle surfaces [40] to grow poly(methyl methacrylate) brushes.

Another strategy to photograft polymers on different substrate is to anchor on the surface thiol groups, by a simply silanization of the surface with alkoxy-functionalized thiol. Under UV-light thiyl radicals are generated from the thiol groups and these radicals are able to initiate free-radical chain growth polymerization from the surface. This approach has been used by Mostegel and colleagues to photopattern planar surfaces with polyethylene (glycol) brushes and biomolecules. When thiol functionalities are exposed to UV-light in presence of oxygen, UV-induced photooxidation of the thiol occurs which yields to sulfonate groups. These sulfonic acid groups were used for immobilization of amino-functionalized biomolecules while the intact thiol groups were used to induce a photografting polymerization of polyethylene (glycol) [41]. Razza *et al.* [42] employed a similar strategy to fabricate Janus particles from micrometric thiol-functionalized silica particles. A *photografting-from* polymerization was initiated from thiol-functionalized silica particles partially masked in colloidosomes structures. The photogenerated thiyl radicals initiated the photografting of poly(ethylene glycol) brushes, while the unreacted thiol groups were employed to bind photogenerated gold nanoparticles.

The group of Bowman reported the use of thiol surface functionalities to photoactivate the formation of PEG-brushes. The photogenerated thiyl radical adds across the carbon-carbon bond of the m-PEGMA to form a carbon-sulfur bond and carbon radical. The just formed carbon radical can add to another m-PEGMA molecule and propagate leading to the formation of



**Figure 8.** Structure of hyper branched TX and initiation mechanism. Reproduced and adapted from ref. [40].

PEG-brushes [43–45]. Also some ketones and aldehydes were reported to undergo hydrogen abstraction from substrate upon UV-irradiation. So, in a very similar way as in the case of BP these compounds could be used to promote *photografting-from* process, where the monomer is added on the radical generated on the surface [46].

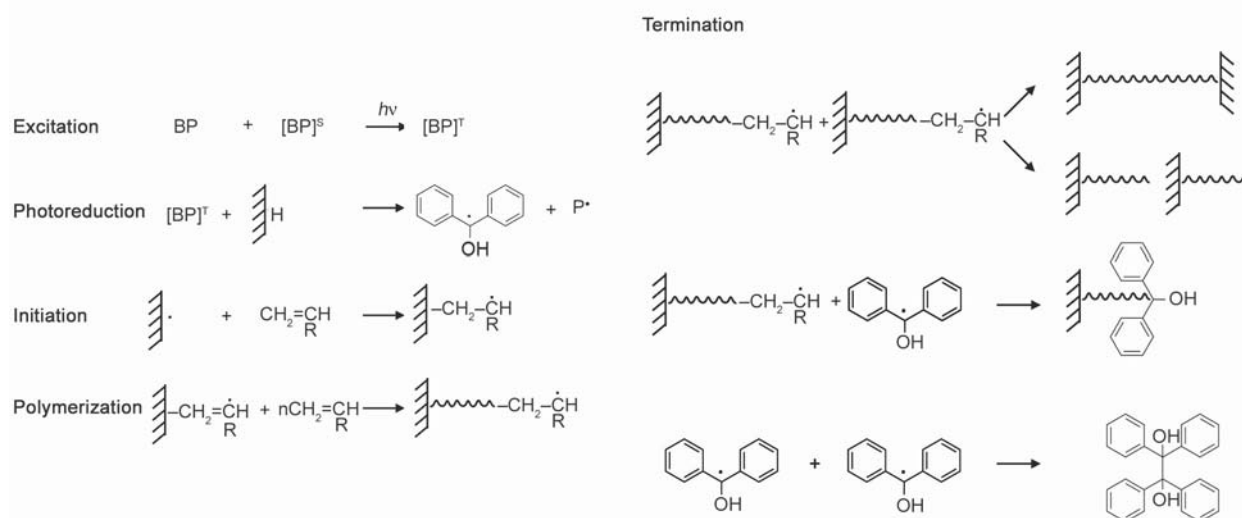
### 3. Control photografting

Living photografting polymerization was reported for the first time by Yang and Ránby [47] that found the possibility to control the radical chain grown polymerization allowing to control the length, composition, and the distribution of the grafted chains on the surfaces. The suggested strategy occurs in two steps: in the first step dormant end groups are covalently attach on the surface of the substrate by photografting monomer solutions containing BP, which introduces graft chains end-capped with semibenzopinacol groups. In the second step living radical graft polymerization of monomers is performing by re-activating the dormant end groups. The above procedure is schematized in Figure 9.

Bowman *et al.* [48] investigated the effect of the principal factor affecting sequential photoinduced grafting polymerization. It was found that the graft polymerization rate of acrylic acid increases linearly with increasing surface initiator concentration, and the formation rate of the surface initiator follows a decreasing order dependent on solvent: benzene > chloroform > hexane > methanol > cyclohexane > dimethyl sulfoxide.

Benetti *et al.* [49], as well as Tazaki and Otsu [50] reported the use of ‘photo-iniferters’ (*initiator*, *transfer agent*, and *terminator*) chemical bonded on the substrate. Under irradiation the ‘photo-iniferters’ yields a pair of radicals: the reactive one can initiate monomers to produce a polymer end radical; the less reactive one cannot initiate the polymerization of monomers, but prefers to terminate the growing polymer chains, forming dithiocarbamyl end-capped chain which can be dissociated again to form a radical pair by UV radiation, generating a living/ control polymerization.

Heeb *et al.* [51] reported the fabrication of a thin layer of poly(methacrylic acid) on silicon substrates by controlled photografting strategy. A photoiniferter with a silane functionality, *N,N*-(diethylamino) dithiocarbamates (trimethoxy) silane, was immobilized on the surface via conventional condensation reactions with surface silanols. After photografting, no special washing was required because the homopolymerization of the monomer was completely suppressed by using LEDs light source (cold light to avoid unwanted thermal polymerizations) with a proper wavelength (selected in the region where the monomer does not absorb) [51]. By using the same photo-iniferter, Spencer’s group showed how thin films of poly(acrylamide) (PAAm) brushes can be grown from iniferter-functionalized silicon substrates by UVLED-initiated photopolymerization. The adopted photografting strategy allowed the controlled fabrication of very thick films (up to 1  $\mu\text{m}$ ) in an aqueous environment. This was carried out over a period of less



**Figure 9.** Scheme of the proposed living-control *photografting-from* method. Reproduced and adapted from ref. [47].

than 1 h of polymerization and in the absence of side reactions [52].

#### *Self-initiating photografting*

There are some monomers, such as Maleic anhydride (MAH) which can undergo in a photografting polymerization even in the absence of any photoinitiator. In fact, under UV-irradiation, MAH molecules produce excimers that are able to abstract hydrogen from the backbones of the substrate and form surface free radicals which could consequently initiate graft polymerization and homopolymerization of MAH as well as other monomers [53]. With LDPE as the substrate and after UV irradiation, the conversion percentage and grafting efficiency of MAH can reach nearly 80 and 70%, respectively.

Another important example of self-initiated photografting is shown when poly(ether sulfone) ultra-filtration membrane are irradiated in the presence of *N*-vinyl-2-pyrrolidinone. The resulting grafted membrane showed a severe loss of protein rejection [54]. The *grafting-from* method is activated due to the use of very low wavelength, where the polymer absorbing generating free-radicals on its surface [55].

Jordan and coworkers [56, 57] reported in several work the photogeneration of polymer brushes by direct self-initiated photografting. This occurs by hydrogen abstraction by a radical mechanism under the UV-illumination via from glassy carbon and silicon carbide [58] substrates. They demonstrated that the presence of C–OH functionalities onto the surface is a crucial parameter for the hydrogen abstraction.

Similarly, Steenackers *et al.* [59] demonstrated that uniform of patterned polymer brushed can be grown from graphene without the use of any initiator and by simply UV-irradiation. They proved that photopolymerization occurs at existing defect sites. Polymerizations were performed with a wide range of monomers (including styrene, methyl methacrylate (MMA), *N,N*-dimethylaminoethyl methacrylate (MAEMA), methacrylateoethyl trimethyl ammonium chloride (METAC), and 4-vinyl pyridine). Additionally, they demonstrated there is non-detectable disruption of the basal plane conjugation of graphene after the photografting.

Shiojima and colleagues reported a highly efficient methodology for preparing a poly(2-methacryloyloxyethyl phosphorylcholine) layer on the surface of poly(ether ether ketone) (PEEK) by photoinduced and self-initiated graft polymerization. PEEK has

diphenylketone unit in the main chain which is similar to the structure of benzophenone. Therefore, when photoirradiated, activation of diphenylketone units in the PEEK chain is induced and semibenzopinacol radicals are formed. These radicals can initiate polymerization of surrounding monomers at the PEEK interface. In the study, the effects of inorganic salt addition (LiCl, NaCl and KCl) was evaluated in terms of increase in polymerization rate. These findings can be explained considering the ionic hydration of the 2-methacryloyloxyethyl phosphorylcholine monomer which is translated in a monomer concentrating effect [60].

A mussel-inspired photografting on colloidal spheres was reported from Jia's lab. Monodispersed SiO<sub>2</sub> spheres with an average diameter of 220 nm were coated with a thin layer of polydopamine. They demonstrated that surface-initiated polymerization reactions can be carried out on polydopamine (PDA)-coated surfaces via a simple surface modification approach. Based on a photopolymerization without adding any photoinitiator or any photosensitizer. In their study, thermally-responsive poly(2-(dimethylamino) ethyl methacrylate) polymer were grown from the polydopamine layer [61]. The same group, in a similar approach, reported the fabrication of self-induced photografting after depositing a thin layer of green tea polyphenols (TP). Indeed, the UV-irradiated generates on the TP surface, surface-bound radicals which can be used for a photoinduced polymerization. When compared with polydopamine-coated surfaces, green tea polyphenol layers were typically colorless instead of dark-black which can be a plus in some applications [62].

#### **4. Conclusions**

In this review, we have shown the important feasibility of *photografting-from* methods to properly functionalize any type of surface. We have discussed the photoactivated *grafting-from* process either using a photoinitiator, able to abstract hydrogen from the surface, or by using functionalized photoinitiators anchored on different substrate and ready to photoactive radical chain grown polymerization. Attention has been devoted to the controlled photografting methods which allow to control length, composition, and the distribution of the grafted chains on the surfaces.

This review aims to stress the importance of the *photografting-from* methods to control the surface of different substrates, achieving a critical view of



the most important contribution in this field to have the tools to properly use the photografting reaction.

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