

## Feature Article

# Photo-induced living/controlled surface radical grafting polymerization and its application in fabricating 3-D micro-architectures on the surface of flat/particulate organic substrates

Yuhong Ma<sup>a</sup>, Lianying Liu<sup>a</sup>, Wantai Yang<sup>a,b,\*</sup>

<sup>a</sup>Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China

<sup>b</sup>State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

## ARTICLE INFO

## Article history:

Received 22 March 2011  
Received in revised form  
15 July 2011  
Accepted 20 July 2011  
Available online 30 July 2011

## Keywords:

UV light  
Living/controlled polymerization  
Graft polymerization  
Polymer brush  
Particles

## ABSTRACT

This feature article covers the fundamental chemistry and applications of photo-induced living surface grafting polymerization. The mechanism of activation of inert alkyl C–H bonds of polymer substrates, the structures of the active free radical and reversible dormant species, the modes of the grafting chain growth (including linear, branched and cross-linked variants), and the role of spatial effect are discussed. Two technologies, i.e., 1-step and 2-step processes, their features and applications in fabricating polymer brushes with precisely controlled patterns, desired functions, branched and block grafting chains on planar substrates, and polymer lamination are presented. The fabrication of 3-dimensional covalently bonded polymer particles, such as nano-sized polymer particle monolayers (with uniform and bimodal distributions), discrete solid and hollow polymer particles of micrometer size, and multilayer polymer particles on polymeric substrates are also introduced. In the last part, the application of photo-induced living surface grafting polymerization in non-planar surface modifications, such as the preparation of core-shell polymer particles, Janus particles and cross-linked hydrogels with hairy polymer chains is summarized.

© 2011 Elsevier Ltd. Open access under [CC BY-NC-ND license](http://creativecommons.org/licenses/by-nc-nd/3.0/).

## 1. Introduction

### 1.1. Living polymerization; history and concept

Since the discovery of living anionic polymerization by Michael Szwarc more than 50 years ago [1], the technology has been successfully exploited for preparing polymers with designed architectures, narrow molecular weight distribution and functionalities. For example, styrene-*b*-butadiene-*b*-styrene has served as a thermally reversible elastomer in which the polystyrene blocks were distinct small discontinuous microphases acting as cross-linking sites for the continuous polybutadiene phase [2]. Szwarc et al. [3] introduced the concept of “dormant polymers” to account for the fact that the living ends can be shielded from termination with a protecting molecule. Since then, living polymerization, also presently known as controlled/living polymerization, has been expanded to ring-opening [4], cationic [5] and free-radical systems

[6,7]. Although the mechanism of the above-mentioned polymerizations is different, the mediation of initiation and propagation rates depends on a dynamic equilibrium between the growing chain and dormant species. These technologies have opened a new avenue to prepare well-defined polymers with precisely designed molecular architectures and nano-structured morphologies, and are considered to be the foundation of polymer nano-technology [8–13].

Indeed, approx. more than 70% of vinyl polymers are produced by conventional radical polymerization due to the technique's versatility that is available to a wide variety of monomers, its tolerance of unprotected functionality in monomers and solvents, its compatibility with process conditions and its cost efficiency [14]. The conventional free radical polymerization consists of four elementary reactions: (1) slow initiation ( $k_d < 10^{-5} \text{ s}^{-1}$ ), (2) fast propagation ( $k_p \approx 10^3 \text{ mol}^{-1} \text{ L s}^{-1}$ ), (3) very fast termination between growing radicals ( $k_t \approx 10^7 \text{ mol}^{-1} \text{ L s}^{-1}$ ), and (4) chain transfer reactions (usually less important unless transfer agents are added) [15]. The average life of a propagating chain is typically on the order of a second, during which the initiation, propagation, and termination take place, yielding a dead chain with a degree of polymerization of approx. 1000–10000 [12,16].

\* Corresponding author. State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China. Tel./fax: +86 10 64416338.

E-mail address: [yangwt@mail.buct.edu.cn](mailto:yangwt@mail.buct.edu.cn) (W. Yang).

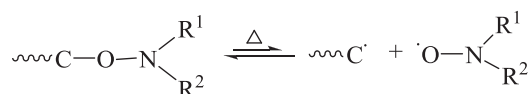
As early as in 1936, Bachmann and Wiselogle [17] stated correctly that the selective unsymmetrical coupling reaction involving stable or persistent free radicals and transient radicals. Perkins [18] explained the unusual product distributions of phenylations of aromatic compounds when phenylazotriphenylmethane was used as a thermal phenyl radical generator. The pioneering work regarding living free radical polymerization came from Otsu and Yoshida [19,20] with name as **iniferter** (initiator—transfer agent—terminator), which photolytically dissociated into a reactive carbon-centered radical and a relatively stable dithiocarbamyl radical in 1982. Then they proposed the possibility of a stepwise growth that would lead to molecular weight control. Iniferter can be classified into several types: thermal or photoiniferters; monomeric, polymeric, or gel iniferters; monofunctional, difunctional, trifunctional, or polyfunctional iniferters; monomer or macromonomer iniferters; and so forth. These not only lead to the synthesis of various monofunctional, telechelic, block, graft, star, and cross-linked polymers [21], but also, especially for photoiniferter system, found number of applications in preparing various polymer brushes [22–33].

In 1985, Rizzardo et al. [34] filed a patent concerning the use of alkoxyamines as initiators, presently denoted the TEMPO system, for living radical polymerization of styrene. The first breakthrough was reported by Georges et al. [35] who found that polymerizations controlled by nitroxide could also be initiated by a conventional initiator in the presence of the persistent radical. Subsequently, three independent groups, Sawamoto et al. [36], Wang and Matyjaszewski [37], and Percec and Barboiu. [38] reported the first successfully performed living/controlled free radical polymerizations almost at the same time in 1995. Some three years later, another robust living/controlled free radical polymerization, known as reversible addition–fragmentation chain transfer (RAFT) polymerization, was invented by the CSICO group [39,40].

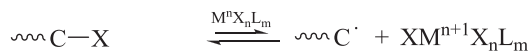
The living/controlled free radical polymerization systems are based on the transiently fast and reversible activation of the dormant species as shown in Scheme 1. It is common that all these living/controlled radical polymerizations are based on a dynamic equilibrium between propagating carbon-center radicals and various types of C–X (X = S, O, N, Br, Cl, I, etc.) bond dormant species. It is not surprising that the chemoselectivity, regioselectivity and stereoselectivity in living/controlled radical polymerization are similar to the conventional radical polymerization due to its nature [12,41–50].

Among available living radical polymerization techniques, the most robust and versatile ones are ATRP/Metal-Catalyzed and RAFT strategies. However, further efforts are obviously needed to address

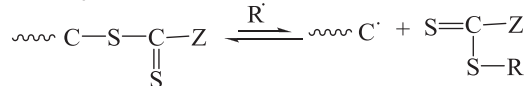
#### NMR or SFRP



#### Metal-Catalyzed Living Radical Polymerization or ATRP



#### RAFT or MADIX



**Scheme 1.** Representative controlled/living radical polymerizations based on modes of dormant and growing species. Adapted with permission from Ref. [41]. Copyright [2009] American Chemical Society.

the cost-inefficiency of these methods, which hinders their industrial application in the production of commodity polymers. Nitroxide-mediated or stable free radical polymerization (NMP or SFRP) systems require high temperatures and demonstrate very slow polymerization rates, which results in low molecular weight products. For ATRP/Metal-Catalyzed reactions, the removal and recycling of the metal catalysts are still a true challenge. When it comes to RAFT, the color of the produced polymers and the unpleasant odor of the chain transfer agents are drawbacks. In addition, there exist other challenges when applied to highly reactive monomers, water-soluble monomers and heterogeneous systems.

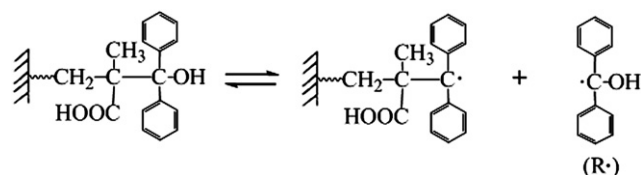
#### 1.2. Photo-induced living/controlled radical surface grafting polymerization

The photoreduction of aromatic ketones leads to the formation of a radical derived from the hydrogen donor and a radical produced from the carbonyl compound (ketyl type radical) in the presence of hydrogen donors. The radicals derived from the hydrogen donors are capable of initiating free radical polymerization of vinyl monomers. Due to their steric hindrance and the delocalization of an unpaired electron, ketyl radicals are preferable for terminating the growing species by coupling reactions other than the addition to vinyl monomers. Based on this chemistry and the liable bond of the end groups produced by the termination, Yang and Rånby elegantly designed a photo-induced living/controlled radical grafting polymerization on the surface of polymer materials [51]. With benzophenone as a photoinitiator, the smibenzopinacol free radical ( $\text{R}\cdot$ ) played the role of the persistent radical to mediate the polymer chain growth (Scheme 2).

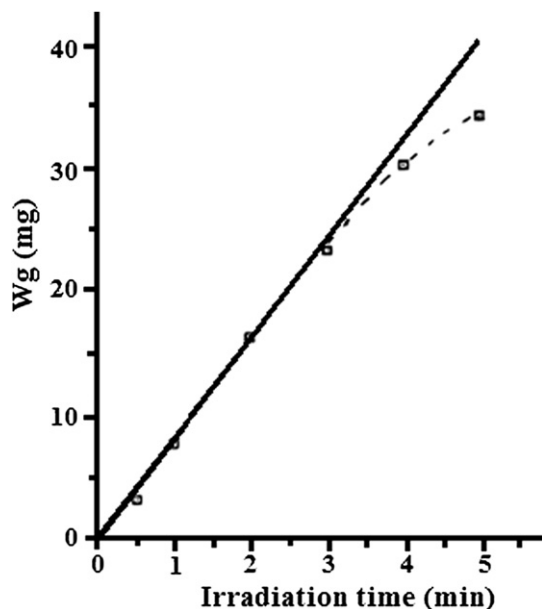
Similarly to the other living free radical polymerization systems, the weight of the grafting PMMA chains increased almost linearly with the irradiation times as shown in Fig. 1.

Very recently, Kyomoto and Ishihara [52] found that the benzophenone moiety in poly(ether ether ketone) (PEEK) polymer chain could act as a photoinitiator during graft polymerization under UV irradiation and named it as “Self-Initiated Surface Graft Polymerization”. This technology was successfully used to graft an antibiofouling and highly hydrophilic high-density nanometer-scaled layer of poly(2-methacryloyloxyethyl phosphorylcholine) onto the PEEK, which showed considerably lower bovine serum albumin absorption ( $0.05 \text{ mg/cm}^2$ ) compared to that of untreated PEEK ( $0.55 \text{ mg/cm}^2$ ) [53].

Contrary to the homogeneous system, the mobility of the graft chains is confined by the substrate. In this case, the coupling reaction mainly takes place between the growing chain free radical and the stable ketyl type radical and produces C–C centered dormant species that can be reactivated by either a photo or a thermal stimulus to build a dynamic equilibrium. Comparatively, the chemistry of this photo-induced living grafting polymerization has the following unique features: (1) the C–H bonds of the polymer chains can be directly transferred into liable C–C bond dormant species in the presence of commercial photoinitiators



**Scheme 2.** The equilibrium of the active and dormant species of photo-induced living surface grafting polymerization.



**Fig. 1.** Relationship between the increasing weights ( $W_g$ ) of the LDPE functional film II (The structure showed in Scheme 2, Left, with semibenzopinacol moiety) and the UV irradiation time at 50 °C with MAA as the monomer. Reprinted with permission from Ref. [51]. Copyright [1996] American Chemical Society.

only; (2) chain growing *via* the reversible deactivation/activation of the liable C–C bonds; and (3) the possibility of activating dormant species by either photolysis or thermolysis.

Besides applications in surface grafting polymerization, efforts have also been devoted to exploiting the photo-induced living free radical polymerization to prepare block polymers in homogeneous system [54]. The chain propagation free radicals generated by addition of this kind stable radical to the monomer cannot be totally eliminated due to the high activation energy of the C–C bond breakage. Therefore, photo-induced living/controlled radical polymerization is slightly weak in terms of the control of the polymerization. However, it has unique applications in confined systems, such as the surfaces of solid substrates, especially since there is no need to introduce initiator to the surface *via* a multi-step reaction. Most importantly, without the limitations of the other living/controlled free radical polymerizations, it is more likely to be suitable for industrial applications in surface functionalization and lamination.

So far, there have been many state-of-the-art reviews on the above-mentioned living/controlled free radical polymerization, for example, iniferter [21], ATRP [12,42–44], transition metal-catalyzed living radical polymerization [45,46] and RAFT [48–50]. This feature article primarily focuses on the chemistry of photo-induced living radical graft polymerization in confined spaces and its applications in the fabrication of complex architectures.

## 2. The chemistry of photo-induced living/controlled free radical surface grafting polymerization

Since the realization of the photo-induced living/controlled surface grafting polymerization in 1996, the research in our lab has been continuously devoted to its fundamental chemistry and applications. Studies include (1) extending the dormant activation from UV light to heating and visible light [55], (2) offering various functional groups with precisely designed patterns to the planar polymer substrates *via* photo-induced grafting polymerization; (3) preparing functional polymer particles, and (4) introducing

functional grafting chains to the surface of polymer particles. These achievements have not only contributed to the development of the living/controlled free radical polymerization but have also made it a powerful tool tailoring the surface properties of polymer materials. Fundamentally, the photo-induced living/controlled free radical surface graft polymerization consists in four fundamental steps: (1) the formation of the initiating free radicals, (2) chain propagation, (3) chain transfer and (4) termination. The discussion in this section is focused on these aspects, especially the *in situ* transfer of the inert C–H bond into dormant species of growing chains under photo-irradiation.

### 2.1. The *in situ* formation of growing chains and dormant species via the C–H bond transformation under UV irradiation

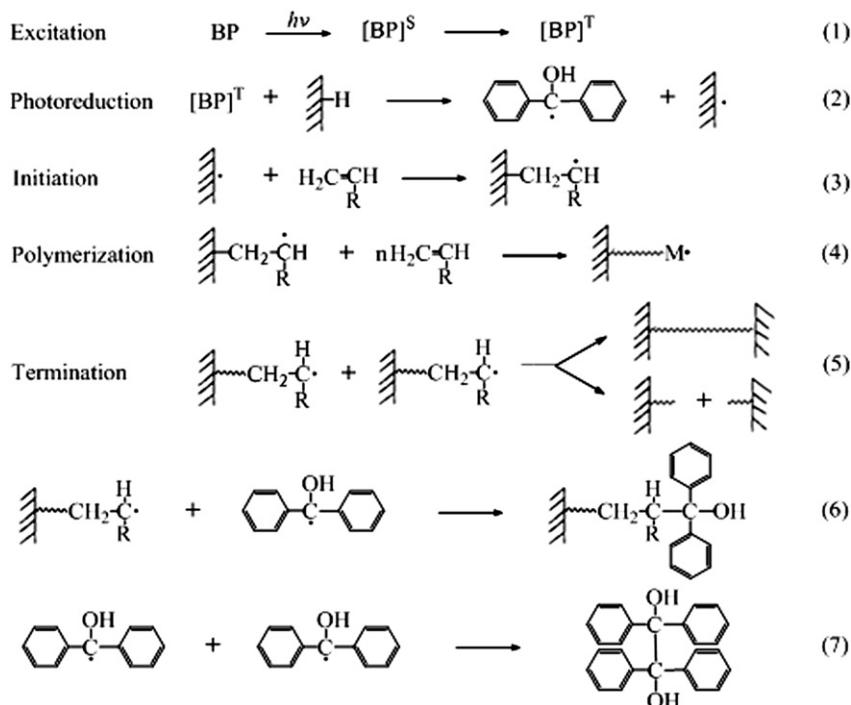
Generally, free radical photoinitiators are classified into two categories: of unimolecular fragmentation type and of hydrogen abstraction or photoreduction type. The former dissociates into two radicals under UV irradiation and is mainly used in UV-curing applications. The latter forms macromolecular free radicals and is widely utilized in polymeric material modification and functionalization. However, conventional photografting has often resulted in the generation of significant amounts of homopolymer and cross-linked structures.

The photo-induced living/controlled surface-grafting polymerization consists of two steps: (1) the aromatic pinacol moiety, which may function as a precursor of the stable or persistent free radical, is covalently bonded to the end of the grafting chain by the coupling reaction of the semibenzopinacol free radical with the propagating radical, and (2) the bonded dormant group is then activated by photo-irradiation or heating to trigger the grafting polymerization (displayed in Scheme 3).

It has also been demonstrated that benzophenone, xanthone, acetophenone and 9-fluorenone are efficient photografting initiators for obtaining thick grafted layers, while anthraquinone, 4,4-dichlorobenzophenone, 4-benzylbenzophenone, benzoylformic acid and biacetyl are suitable photoinitiators when one desires thin grafted layers [56]. A high triplet state energy, a strong UV absorption, a stable molecular structure and a low initiating reactivity of the resulting ketyl free radicals are critical factors when selecting photoinitiators. In addition, the benzophenone moiety in polymer chain could also trigger a “Self-Initiated Surface Graft Polymerization” under UV irradiation [52,53].

The above-mentioned photo-induced living surface grafting polymerization is usually called the 1-step process. Based on the above findings, Bowman et al. [57] further developed a sequential photo-induced living graft polymerization, denoted the 2-step process. In the first step, benzophenone abstracts hydrogen from the substrate to generate surface radicals and semipinacol radicals, which couple to form surface photoinitiators in the absence of monomer. In the subsequent step, the monomer solutions are added to the active substrate, and the surface initiators trigger the graft polymerization under UV irradiation. Fréchet et al. [58] ever evaluated the effect of the 1-step and 2-step grafting process in detail on the performance of the surface-modified macroporous polymer monoliths.

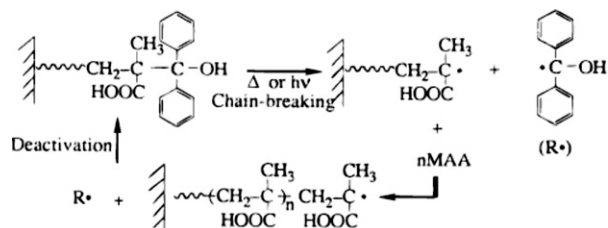
One of the advantages of the 2-step process is its high grafting efficiency, about 4-fold greater than that of the 1-step method for grafting poly(acrylic acid) to polypropylene membranes [57]. In addition, the grafting density and graft polymer chain length can be determined and controlled independently. In summary, the comprehensive fundamental reactions (including the 1-step and 2-step processes) of photo-induced living/controlled grafting polymerization are illustrated in Scheme 4.



**Scheme 3.** Representative controlled/living radical polymerizations based on modes of dormant and growing species. Adapted with permission from Ref. [51]. Copyright [1996] American Chemical Society.

## 2.2. Activation of the dormant species by photolysis and/or thermolysis and the livingness of the reactive species

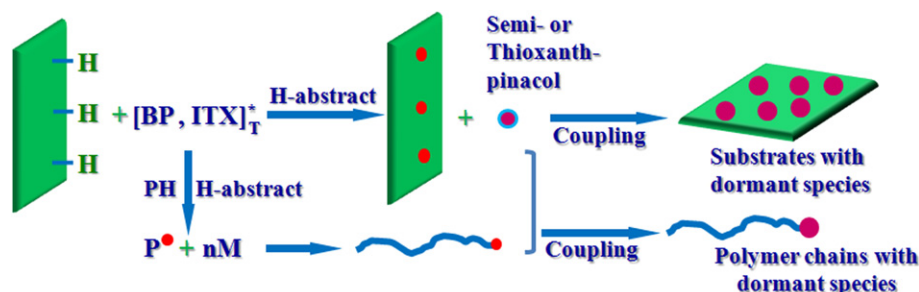
The liable C–C bonds of the dormant species can be activated by both photo-irradiation and heating. The chain ends homolyze into two free radicals, where one is the active chain-growing radical and the other is the persistent semipinacol free radical. The following is the proposed mechanism of the chain growth [51].



In the presence of a vinyl monomer, the chain radicals can add to the monomer and start or continue chain propagation. With methacrylic acid as a monomer, the weights of the grafted polymer increase almost linearly as the graft polymerization proceeds. The

graft polymerization rate of acrylic acid increases linearly with an increasing surface initiator concentration. The rates of the formation of the surface initiator follow a decreasing solvent-dependent order: benzene > chloroform > hexane > methanol > cyclohexane > dimethyl sulfoxide. These observations have been mainly attributed to the relative ability to abstract hydrogen from the solvent and the wettability of the solvent to the substrate. The characteristics of living polymerization of this system in solution grafting polymerization have also been confirmed by Ma et al. [59]. In designed runs, both BP and polystyrene are dissolved in benzene at first; then a thin liquid film of the solution was exposed to UV light, obtaining polystyrene carried semibenzopinacol groups (PS-g-BP). In the second step, poly(ethylene glycol) methacrylate (PEG200MA) and PS-g-BP were dissolved in toluene, and after irradiating, it was found that the molecular weights of modified PS increase with polymerization time and furthermore, the GPC traces clearly showed that the molecular distributions are still symmetrical normal peaks.

There are two factors, i.e., the confined spatial effect and the persistent free radical effect, that account for the photo-induced living grafting polymerization on the surface. The confined spatial



**Scheme 4.** A schematic diagram of the fundamental reactions of the C–H bond transfer chemistry.

effect is due to the fact that one end of the growing chain free radical is tethered to the substrate, thus causing the collisions between the two chain growing free radicals to be greatly minimized. The coupling termination predominately occurs between the persistent free radicals and the chain growing radicals.

However, the confined spatial effect alone is not enough to make a well-controlled living free radical polymerization as demonstrated by the efforts to reduce the termination reactions in emulsion polymerization, where compartmentalization of the radical species prevents the encounter with another growing radical chain in the other particles [60]. During the polymerization process, the semibenzopinacol free radicals act as persistent radicals to maintain the reversible dynamic equilibrium between the growing chains and the dormant species, similar to other living polymerization systems [61]. However, there might be a positive synergistic influence between the spatial effect and the persistent free radical effect which is evidenced by the much more effective control in the surface grafting process as opposed to in solution or for bulk polymerization with this photo-induced system.

The system could also be activated by heating and visible light irradiation. Fig. 2 presents the results when activated by heating. The weight of the grafting PMMA chains increased almost linearly with the reaction times.

With isopropyl thioxanthone (ITX) as the photoinitiator, the living grafting polymerization of GMA activated by visible light was also achieved [55]. Fig. 3(a) presents the change of the GMA grafting degree (Grafting degree =  $(W_2 - W_1)/W_1 \times 100\%$ , where  $W_1$  is the weight of the film after grafting of the “dormant” groups;  $W_2$  is the weight of the film after the grafting polymerization of GMA) with irradiation time, and Fig. 3(b) gives the variation of the average graft polymer chain length with grafting conversion of GMA at various concentrations. It is demonstrated

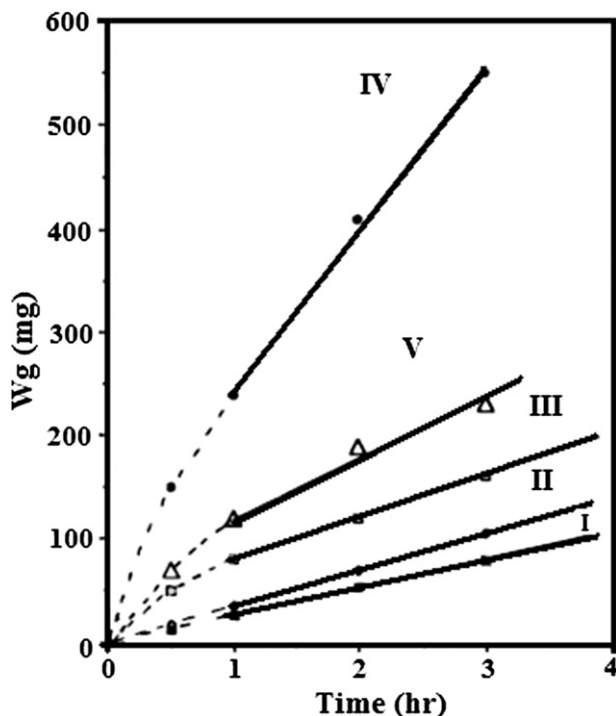


Fig. 2. Relationship of the weight increase ( $W_g$ ) of five functional LDPE films I–V and the polymerization time at 85 °C with MAA as the monomer. Each LDPE film weighed about 250 mg. Reprinted with permission from Ref. [51]. Copyright [1996] American Chemical Society.

that the degree of grafting for PGMA increased gradually with the irradiation. When the irradiation time was greater than 40 min, the curves leveled off. The authors pointed out that this leveling-off could be attributed to the polymerization taking place within a confined space in which the monomer concentration decreased gradually as the polymerization progressed. It is also demonstrated that the average graft polymer chain length increased linearly with the monomer conversion of GMA at a given grafting density of initiator (dormant) groups and a given monomer concentration. This linear relationship indicates a living/controlled polymerization feature.

### 2.3. The branching growth mode of the graft chain

As early as in 1996, Yang and Rånby [62] reported on the lamination of polymeric materials by UV irradiation in the presence of a vinyl monomer and a photoinitiator. They observed that branched polymer chains and cross-linked structures were formed, which were results of the fact that the triplet BP could abstract hydrogen atoms from C–H bonds of the newly formed grafting chains during the grafting polymerization.

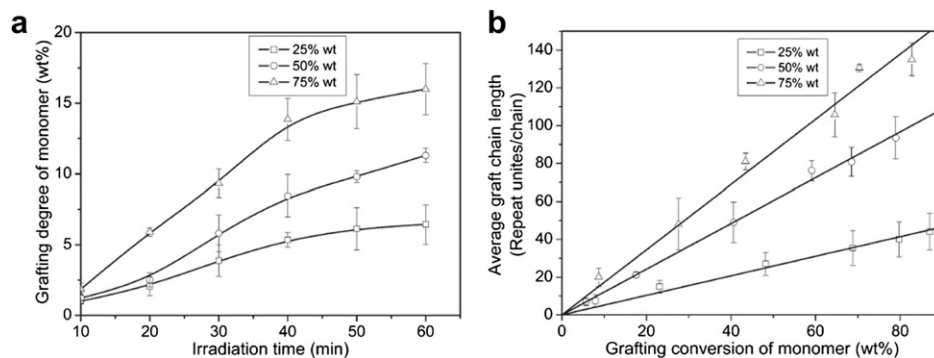
As we known, polymerization of vinyl monomers, in fact, results in the transformation of the C–H bond character from an  $sp^2$  hybrid (unsaturated C–H in monomer) to an  $sp^3$  hybrid (saturated C–H in polymer chain). This transformation causes the C–H bond energy to decrease by about 10 kcal/mol, and finally becomes a potential hydrogen donor to be abstracted by the excited BP as shown in Scheme 5. Scheme 5 also illustrates the branching mode of the polymer chain growth. In the 1-step process, the photoreduction and surface grafting mainly take place at the surface of the substrate. As the grafting polymerization proceeds, the newly formed grafting chains become new hydrogen donors. The triplet BP begins to abstract the hydrogen atom from the newly formed graft chain to generate branching sites.

Branched polymer chains can also be formed by photo-induced homopolymerization. Whenever branched and cross-linked polymers are desired, for example, the lamination 1-step process is a robust tool. Contrary to the 1-step process, the 2-step process involves no free BP to be excited in the grafting process. In this regard, the 2-step process is effective to substantially eliminate the formation of undesired homopolymers and cross-linked or branched grafting chains. In this case, the photo-induced grafting polymerization results in clean and linear grafting chains. The photo-induced grafting polymerization thus represents a unique and simple option to prepare linear and branched grafting polymer chains.

### 2.4. The features of the photo-induced living/controlled grafting polymerization

Living/controlled free radical polymerization techniques, including ATRP and RAFT, have been widely used in surface grafting polymerizations on various substrates such as organic polymer films, polymer particles, inorganic particles and films [50,63]. In practice, it is a prerequisite to have or introduce functional groups onto the surface of substrates by, at first, a multi-step reaction. The process is usually very time-consuming since both the substrates and the initiators or RAFT agents are required appropriate reactive groups.

Unlike the grafting polymerizations via the ATRP and RAFT technologies, the photo-induced process can directly transfer the inert C–H bonds to the liable C–C bonds or grafting chains with reversible dormant groups. With this technique, the graft density and graft polymer chain length can be controlled independently



**Fig. 3.** (a) The grafting degree of the monomer versus the irradiation time and (b) the average graft polymer chain length versus the grafting conversion of monomer at varying GMA concentrations (ethyl acetate as solvent) under visible light irradiation. During the first step, the amount of grafted ITX semipinacol was 0.19 wt% of the blank LDPE film under conditions of 0.5 M ITX in acetone and 180 s of UV irradiation for all experiments. Reprinted with permission from Ref. [55]. Copyright [2009] John Wiley and Sons.

since the initiator formation and graft polymerization can occur separately in successive steps. Furthermore, it avoids the use of additional species on the surface or in the monomer solution and ensures that the grafting polymerization takes place at the surface only when the 2-step process is applied. As the polymerization proceeds, the grafting chains can act as hydrogen donors and generate new active sites to form branched chains. Similar to nature's process, under the activation of UV irradiation and/or heating, the chains progressively grow to prepare the grafting layers with various chain architectures as illustrated in Scheme 6. The polymer chains grow not only from the surface of the substrates but also from the newly grafted chains.

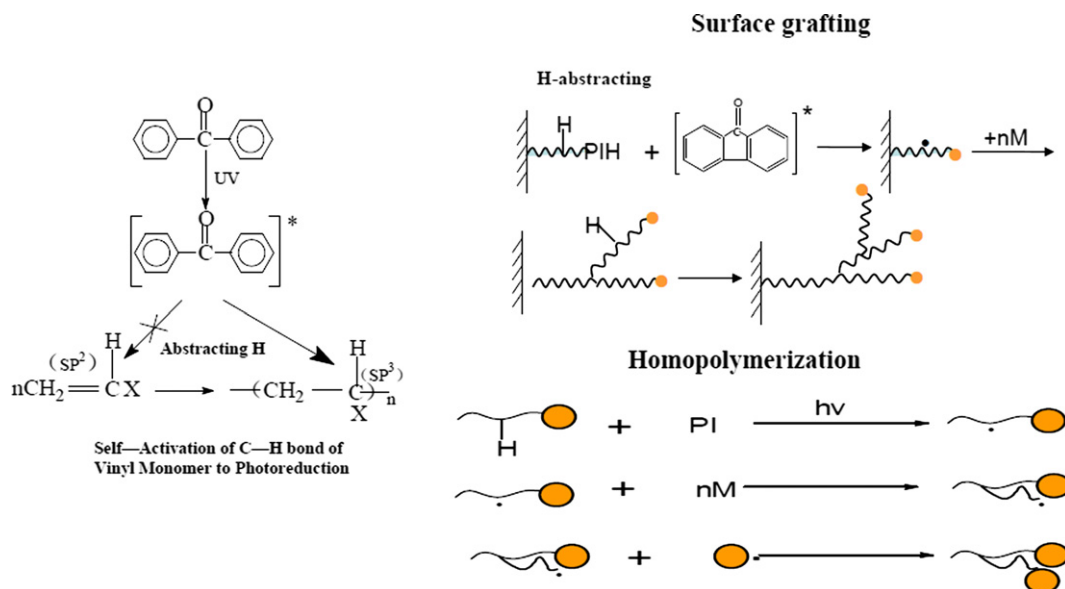
There are even more advantages of photo-induced polymerization. When activated by photo-irradiation, the grafting polymerization can be performed at ambient temperature, which is very helpful for the retention of profiles and the morphology of substrates. Most importantly, the bioactivity of the materials can remain unchanged if the grafting polymerization is activated by visible light. This technology is applicable to materials with C–H bonds or other hydrogen donors in their structures, especially inert polymers such as polyolefins and silicone.

### 3. Applications in fabricating well-defined structures and morphologies

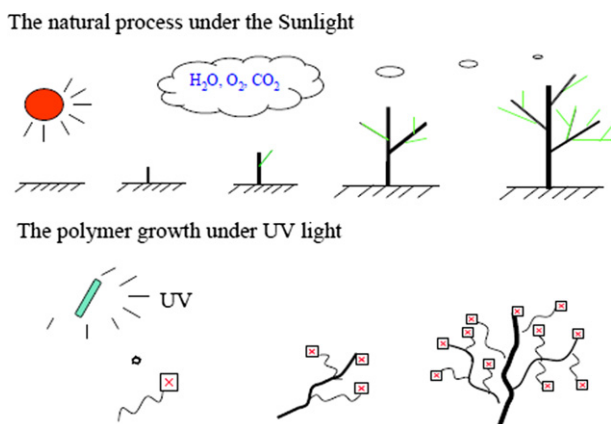
Experimental work has demonstrated that photo-induced living/controlled free radical polymerization is a robust tool for precisely constructing a well-defined architecture on organic substrates containing hydrogen-donor moieties. This section focuses on grafting polymer chains or brushes and particles onto a flat polymeric surface or the surfaces of polymer particles.

#### 3.1. Grafting chains and brushes via photo-induced grafting polymerization from a flat polymer surface

Most polymeric materials, especially the large-volume products such as polyolefin, PET, etc, have a hydrophobic and chemically inert surface. Significant research efforts have been devoted to their surface modification and many technologies have been developed and are applied in various industrial applications. Among these methods, surface graft polymerization offers the possibility of grafting the polymers with a variety of functional groups. The technique has the following advantages: it does not affect the bulk



**Scheme 5.** The mechanism to form branched grafting chains in photo-induced living free radical polymerization (PI is the abbreviation of photoinitiator and PIH is the derivative of PI in reduced form).



**Scheme 6.** The proposed biomimicking growth mode of photo-induced polymerization.

properties of the substrate, it can be performed under relatively mild conditions, it is applicable to various polymer substrates including polyolefins, polyesters, fluoropolymers and conjugated polymers, and it provides a relatively long-term chemical stability, in contrast to physically coated polymer chains. Surface grafting polymerization is usually initiated by chemical treatment, photo-irradiation, high-energy radiation and has been widely used for improving surface tension values [64–69] and adhesive properties [58–79], in modifying or functionalizing membranes [80–106], in laminating polymer films or sheets [62,107–114] and in fabricating medical devices [115–122]. These applications have been well-documented in several reviews [123–127].

The intention here is not to give a comprehensive literature survey of these applications. Instead, the focus is placed on the unique features, which are difficult to achieve by other grafting processes, of photo-induced living grafting polymerization in controlling the grafting structures, morphology and in fabricating complicated patterns and architectures, e.g., polymer brushes with precisely controlled patterns, polymer brushes with desired functions, branched grafting chains and lamination.

### 3.1.1. Polymer brushes with designed patterns

With micro-fabrication and manufacturing becoming an attractive field to both the academic and industrial community, one of the challenges to the surface modification of polymeric materials is to precisely implant different surface chemical functionalities in the specific sections with complex and integrated patterns. It has been found that photo-induced grafting reactions render it possible to precisely control the modified locations, sizes and patterns with a photomask. In addition, the grafting density and chain length can be simply mediated by the irradiation time.

Fig. 4 represents an example of the fabrication of grafting patterns onto an LDPE substrate [55]. The dormant ITXSP group was immobilized onto the LDPE substrate by first using a stripe pattern photomask, and then carrying out reactivation with visible light to initiate the grafting polymerization of glycidyl methacrylate (GMA). When extending the irradiation time, the stripe pattern gradually became clear and dense. These stripes represented the negative image of the photomask reproduced on the substrate. There was no observable overlap of the grafting stripes on the non-irradiated areas, which remains a great challenge for other grafting technologies.

The thickness of the grafting layer increased almost linearly to a maximum of about 980 nm with the irradiation time from 0 to 60 min. It should be noted that this method shows great potential for biology applications. For instance, the thermal and UV sensitive

species can be encapsulated by visible light-induced grafting. It is implied that the dimension sizes, profile of the patterns and locations of the graft chains could be precisely controlled with a photomask in a very simple operation. The livingness of the grafted PGMA layer was demonstrated by the addition of the second monomer styrene to prepare the PGMA-*b*-PS polymer brushes. The FTIR-ATR (Fig. 5) and the readings of contact angles of the grafted films verified the formation of the PGMA-*b*-PS brushes.

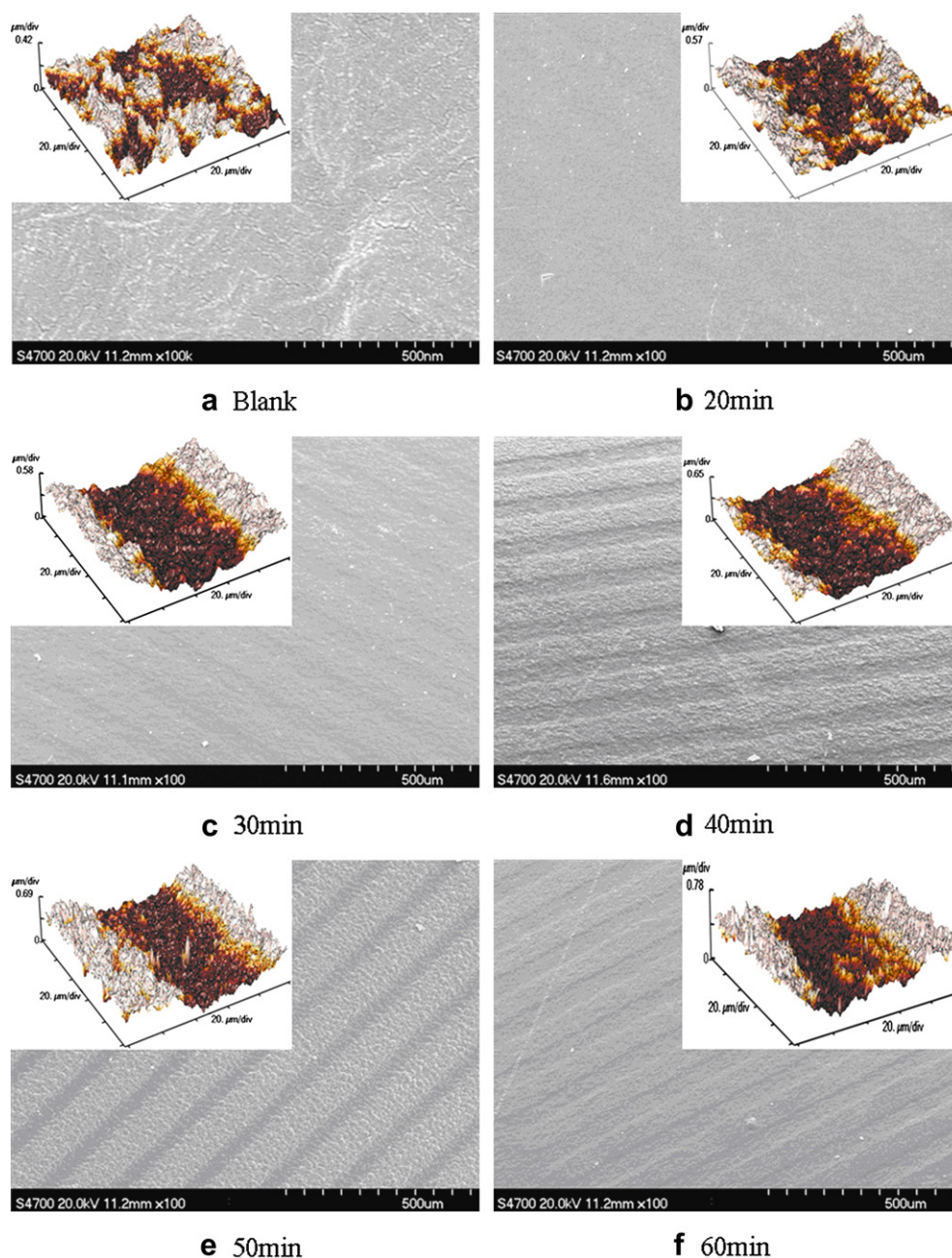
Most recently, Yang et al. [128] reported that a pattern of binary polymer brushes, PAA and PGMA, were prepared *via* consecutive UV-initiated grafting procedures, under the assistance of an *in situ* formed poly(4,4'-bi[N-(4-vinylbenzyl) pyridinium]) (P(BVV)) photomask. The epoxy groups of the PGMA microdomains could be aminated so as to covalently couple biotin, while the PAA microdomains were used for immobilizing immunoglobulin (IgG). The resulting biotin- and IgG-coupled microdomains interacted specifically with their corresponding target proteins, avidin and anti-IgG, respectively, as shown in Fig. 6.

### 3.1.2. Grafting chains with desired functions

As early as in 1994, Nonaka et al. [129] reported thermo-sensitive membranes which were prepared by heterogeneous graft copolymerization of poly(*N*-isopropylacrylamide) (NIPAAm) onto cellophane in a nitric acid solution with cerium ammonium nitrate as an initiator. Yang and Yang [100,130] exploited the application of surface photografting polymerization in the preparing a polyethylene terephthalate track membrane with a thermo-sensitive switching feature by photografting of PNIPAAm. As demonstrated in Fig. 7, the thermo-sensitive property depended significantly on the grafting degree (*Dg*). When the *Dg* was less than 1%, it showed no thermo-sensitivity. When the *Dg* exceeded 1%, the thermo-sensitive valve effect was observed, and at a higher *Dg* (2.48%), the water flux at low temperature (12–30 °C) declined to zero. The temperature window of flux transfer in the range of 30–35 °C was close to the low critical solution temperature of PNIPAAm (33 °C). The higher the *Dg*, the larger was the ratio of flux at 35 °C as opposed to that at 30 °C. A pore-covering mode, as illustrated in Fig. 8, is proposed to explain this phenomenon. At low *Dg*, in the wet state, the water flux decreased slightly and no switching effect appeared since the density of grafted polymer brushes was too low to cover the pores. With the increase of *Dg*, the swelled graft layer became thick enough to block, at least partially, the pores at low temperature. When the *Dg* was greater than a given critical value, the pores could be completely blocked and the flux declined close to zero. Above the critical temperature, the polymer brushes shrank and left a less blocked pore, and the water flux increased.

Similarly, Yang and Yang [101] also reported a pH-switching PET track membrane with a pore-covering structure prepared by photografting of 4-vinylpyridine. The relationship between flux and *Dg* in acidic (pH 2.0) and neutral (pH 6.8) solutions is presented in Fig. 9. In a neutral environment, the fluxes were close to that of a blank membrane and even the *Dg* increased to 2.54%; 90% of the blank membrane flux was still retained. Under acidic conditions, a very low *Dg* of 0.3% was enough to make the fluxes decrease drastically. With the increase of *Dg*, the fluxes in acidic solution were close to zero, and the ratio of fluxes in neutral as opposed to in acidic conditions rose from 20 to 150 when the *Dg* increased from 0.3% to 2.54%. In this respect, a full open/close pH-valve membrane based on pore covering was achieved by the photografting technology.

Moro et al. [115,116] developed a new-concept artificial hip joint system by grafting poly(2-methacryloyloxyethyl phosphorylcholine) (MPC) onto the surface of cross-linked polyethylene (CLPE). The results showed that the graft layer is helpful to reduce wear and suppress bone resorption [115–122,131–134]. The physical and



**Fig. 4.** SEM and AFM micrographs of (a) a blank LDPE film as well as films grafted with PGMA by visible light irradiation through a stripe-patterned mask for (b) 20 min; (c) 30 min; (d) 40 min; (e) 50 min; (f) 60 min. The SEM images in (b) and (c) were obtained after tilting the sample 30°. Reprinted with permission from Ref. [55]. Copyright [2009] John Wiley and Sons.

mechanical properties of CLPE and CLPE-g-MPC had no significant difference. However, an 88% reduction of the friction coefficient was observed, from 0.0075 of the untreated CLPE cups reduced to 0.0009 of CLPE-g-MPC cup. After  $3.0 \times 10^6$  cycles in the hip joint simulator test, there was not observable wear for CLPE-g-MPC cups [117]. It was concluded that the grafted MPC polymer gave a high lubricity only on the surface and has no effect on the bulk properties of the CLPE substrate.

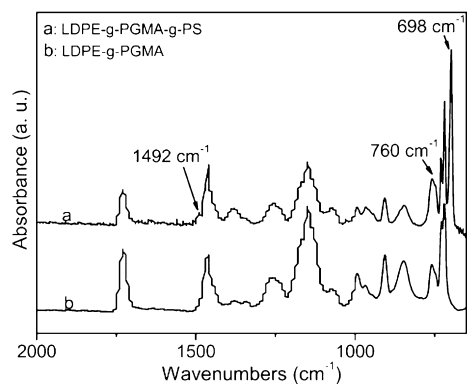
### 3.1.3. Branched grafting chain and lamination

Based on knowledge of the photografting polymerization, Rånby and Yang [107–110] invented a novel technology, which they named “lamination by bulk photografting”, as illustrated in Scheme

7. A thin layer of the monomers (usually acrylic acid or acrylates) containing photoinitiator was sandwiched between two polymeric films after which the assembly was subjected to UV irradiation. The polymerization developed in a successive pattern denoted as S and G and which consisted of respectively a hyperbranched graft macromolecule and a cross-linked macromolecular network obtained by adding multifunctional monomers.

Fréchet et al. [111] also believed that branching and even cross-linking reactions take place when proceeding with a photografting polymerization. At the beginning, only a limited number of polymeric chains grow from the surface. As the polymerization continues, the degree of branching increases since grafting also occurs *via* H-abstraction from the already grafted chains. As the density of chains





**Fig. 5.** FTIR-ATR spectra of the LDPE-g-PGMA film and LDPE-g-(PGMA-b-PS) film. Reprinted with permission from Ref. [55]. Copyright [2009] John Wiley and Sons.

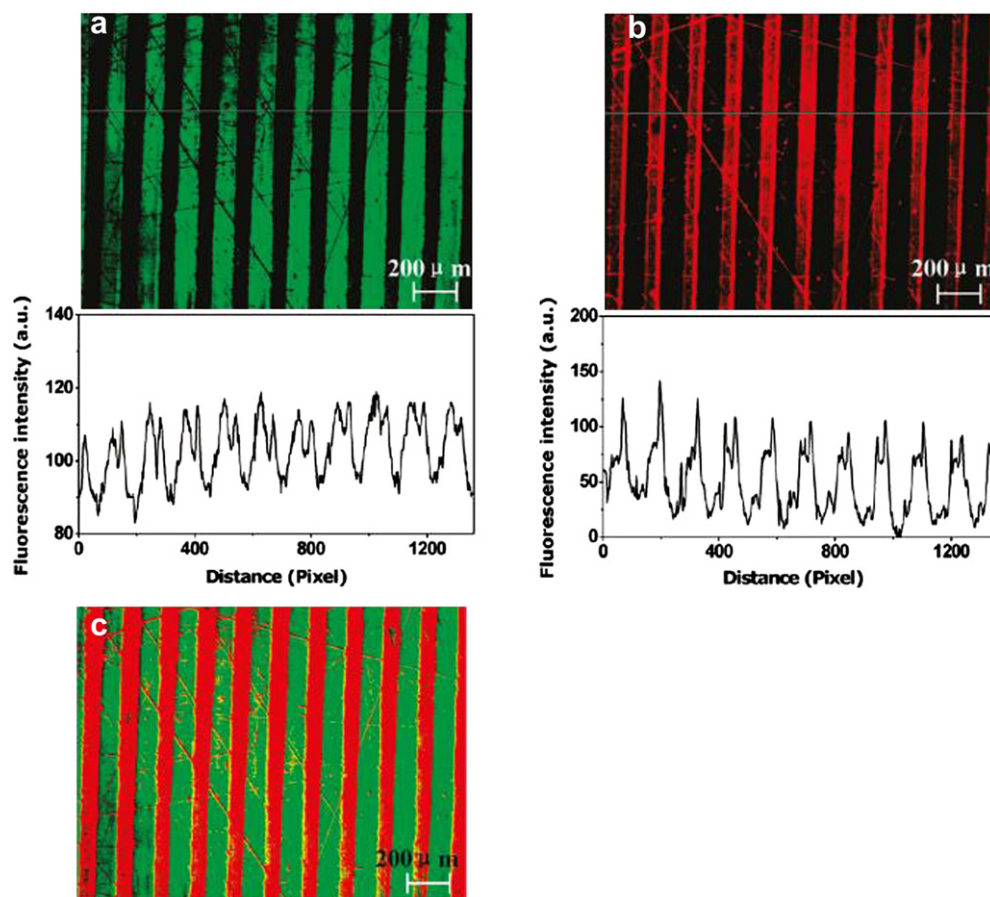
grows, cross-linking becomes increasingly prevalent, and finally, a dense cross-linked polymer network is formed. Considering the nature of the grafting reactions forming a polymer layer cross-linked *via* intermolecular termination reactions of the branched polymer chains, the cross-linking density must clearly depend on the distance between the individual chains. Obviously, the propagating model makes it possible for the grafted branched polymers to reach the scale of the laminate dimension in size.

By ozone-pretreatment of the substrate and then UV-induced grafting polymerization, Kang et al. [112] also demonstrated

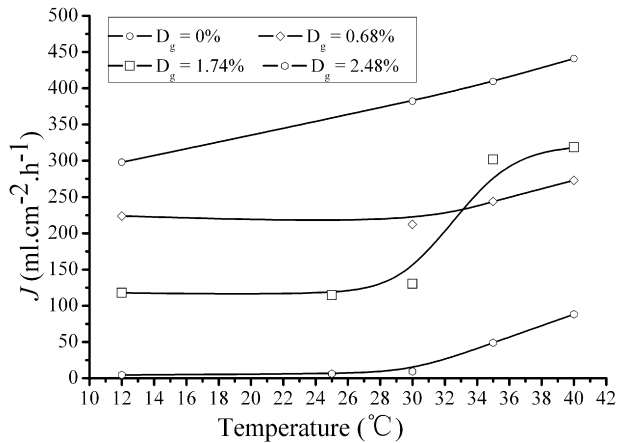
photolamination. Brown and Wang [113] investigated the adhesion mechanism of photolamination of HDPE films and sheets, and it was found that a very good adhesion was achieved with the addition of hydroxyethyl methacrylate or GMA to the acrylic acid monomer. With photolamination, the adhesion between two polymeric films is significantly improved. Research efforts have demonstrated that this is applicable to the lamination of LDPE, HDPE, PP, OPP, PET and Nylon-66. It is reasonable to believe that photolamination could be adapted to any material with liable hydrogen atoms where at least one layer is transparent to UV light.

### 3.2. Fabricating mono- and multilayers of polymer particles on flat polymeric substrates

The morphology of a grafted surface is another interesting topic. Brown and Wang [135] observed the surface microstructure and morphology of an HDPE film photografted with PGMA by AFM. Generally, the surface of the grafted films exhibited a granular structure, and the size of the granules increased linearly with their diameters. Each granule seemed to be a single graft chain bearing a highly branched microstructure. Uchida and Ikada examined the topography of water-soluble chains grafted onto a PET film [136]. However, the morphology of the linear grafting chains might be changed when exposed to solvents and heating. If spherical polymer particles are covalently bonded to the surface of polymer substrates, patterned surface with three-dimensional (3-D) topology would be fabricated.



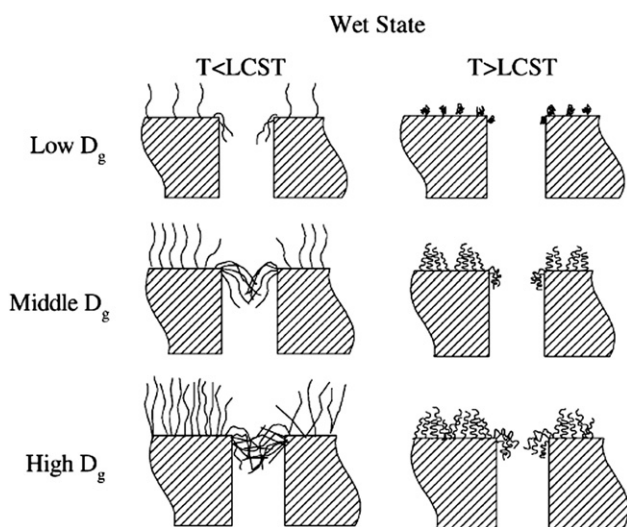
**Fig. 6.** Fluorescent images of the (a) FITC-avidin-coupled regions, (b) rhodamine-anti-IgG-coupled domains of the PAA-anti-IgG/PGMA-avidin surface, and (c) the corresponding false-color overlay of fluorescent images from (a) and (b). Reprinted with permission from Ref. [128]. Copyright [2010] American Chemical Society.



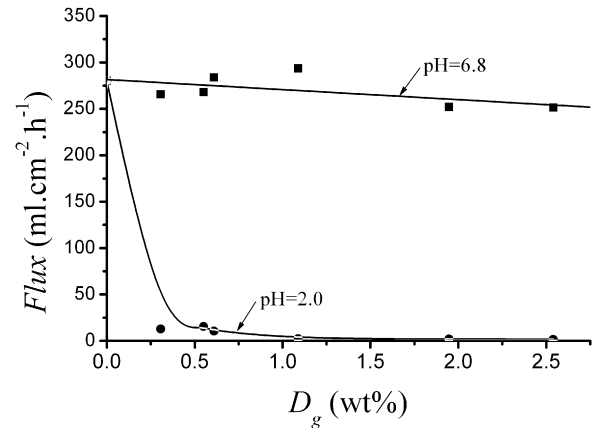
**Fig. 7.** Properties of thermo-sensitive membranes with a pore size of 0.2  $\mu\text{m}$  (without a cross-linking agent, and with a feed pressure of 100 kPa). Reprinted with permission from Ref. [130]. Copyright [2003] Elsevier.

With the great success of the surface photografting polymerization, Yang et al [137–141] conducted a series of investigation with conventional emulsions and microemulsions as grafting media. The formation of solid polymer nanoparticles immobilized on the surface of the polymer substrates was observed. As summarized in Scheme 8, this technology has been successfully exploited to graft large solid polymer particles and hollow particles (Route 1), monolayer particles with bimodal particle size distributions (Route 2), monolayered polymer particles and multilayer polymer particles (Route 3 and 4) with uniform particle size distributions. In short, a pathway to construct a 3-D architecture on polymeric substrates by photografting polymerization has been developed.

In the presence of the amphiphilic monomer *N*-vinylpyrrolidone (NVP) and a microemulsion of MMA and divinylbenzene (DVB), the micrometer-sized solid/hollow spherical particles were grafted onto polymer substrates per Route 1 as illustrated in Scheme 8 by a 1-step photografting polymerization [137,141]. When the concentration of MMA in the microemulsion was 20% (wt), solid particles were obtained. On the other hand, with the concentration



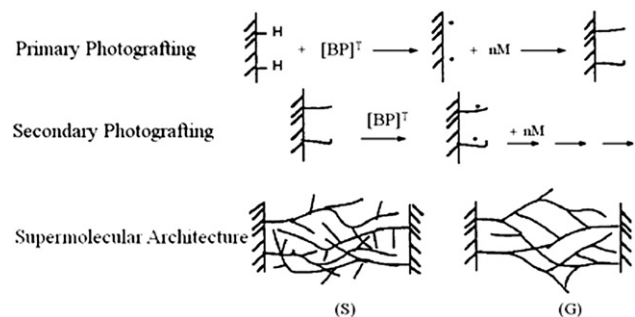
**Fig. 8.** A schematic of grafted thermo-sensitive polymer brushes regulating the filtration property. Reprinted with permission from Ref. [130]. Copyright [2003] Elsevier.



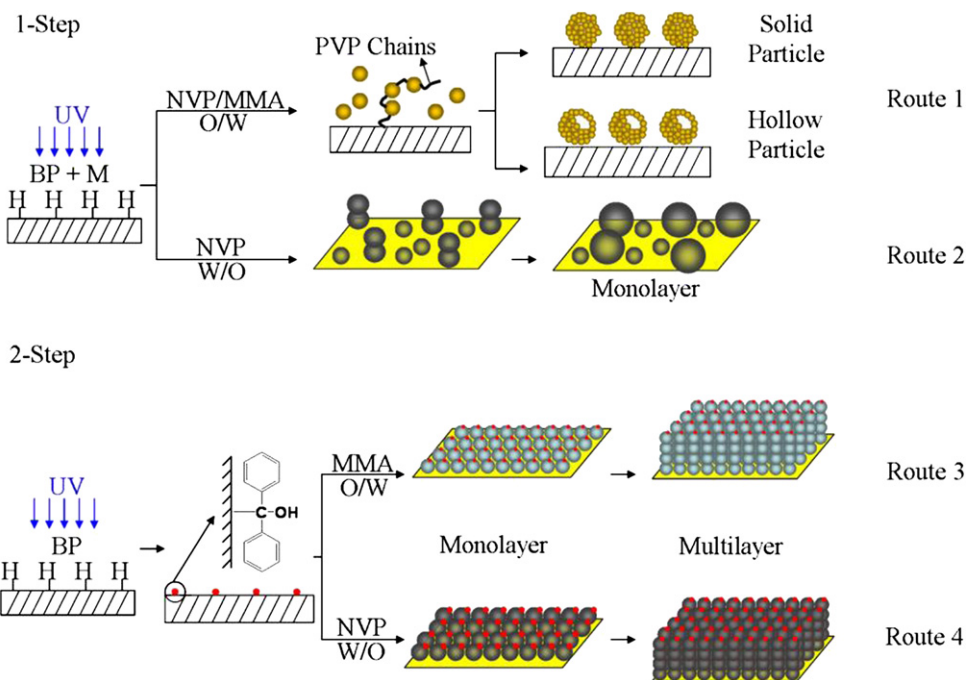
**Fig. 9.** The valve effect of a 0.2- $\mu\text{m}$  grafted membrane with varying  $D_g$  of poly(4-vinylpyridine). Reprinted with permission from Ref. [101]. Copyright [2005] Elsevier.

of MMA reduced to 15% (wt), hollow particles were produced. Both the solid and hollow particles are of tunable sizes in the range of 350 nm–1.3  $\mu\text{m}$ . AFM images revealed that the grafted particles (either solid or hollow) consist of primary nanoparticles linked by polymer chains in a spatial architecture. The microemulsion consists of the oil phase of MMA and a small amount of the cross-linker monomer DVB, an amphiphilic monomer NVP and a cationic surfactant in the water phase. Under UV irradiation, the photoreduction between BP and triethylamine may occur at the interface of water/oil phases to yield free radicals that initiate the polymerization of monomers in one of the phases. If the initiation takes place in the water phase, the produced PVP chain radicals form micelles because of the good affinity of PVP to the cationic surfactant (CTAB), and cross-linked PMMA nanoparticles are thus created by MMA microemulsion polymerization. Alternately, MMA/DVB could possibly be initiated first during the polymerization. In the microemulsion polymerization, the propagating radicals diffuse to the interfaces of the micelles, then initiate the polymerization of NVP, and continuously re-enter other micelles. Whichever monomers are initiated, spherical solid or hollow supramolecular polymer particles can be formed by repeating the process, where nanometer-scale cross-linked primary PMMA particles serve as building blocks and are covalently connected by PVP chains.

When NVP/*N,N'*-methylene bisacrylamide (MBA) inverse microemulsion was used in a 1-step surface photografting process (Route 2), the grafting particles were bimodally dispersed in sizes [139]. In this grafting system, both NVP and its polymer, PVP, are amphiphilic. The amphiphilicity of the PVP chains in the micelles would make them easy to extend out of the micelles, causing them



**Scheme 7.** Primary photografting, secondary photografting, and supermolecular architecture in lamination by photografting. Reprinted with permission from Ref. [107]. Copyright [1997] John Wiley and Sons.



**Scheme 8.** An illustration of the fabrication of 3-D architectures on polymeric substrates.

to aggregate with others nearby. Hence, there are chances of forming the special quasibimodal structure with larger particles of more than 100 nm in size. On the other hand, the primary particles have nanometer sizes, and are therefore prone to self-aggregation. Consequently, a quasibimodal structure, with particles of about 110 and 45 nm, is formed. It is very interesting that, with the addition of cross-linking monomer MBA in the inverse microemulsion, the contact angle of the modified substrate is reduced to about 3–5° and that there is no significant degradation for a time period of three months. The morphology of the nanoparticles contributes to this significant difference. In comparison, the contact angle is reduced to 23–28° with grafting NVP inverse microemulsion only.

With a 2-step photografting polymerization with an opaque emulsion of MMA and the cross-linker DVB, a monolayer of cross-linked PMMA particles and multilayer particles with a uniform size distribution has been grafted onto polymeric substrates (Route 3) [137,138]. The results showed that the monomer conversion was in the range of 15–55%, that the grafting efficiency ( $GE\% = (W_g/W_p) \times 100\%$ , where  $W_g$  the weight of grafting nanoparticles, and  $W_p$  the weight of the whole polymer) was about 80%, that the grafting yield reached 5%, and that the thickness of the graft layer could be controlled in the range of 0.09–1.5  $\mu\text{m}$ . AFM micrographs demonstrated that the graft layer was piled up by nanoparticles (about 30–50 nm in diameter), which were linked together and tied to the substrate surface with covalent bonds. However, with NVP/MBA inverse microemulsion as the reaction media in a 2-step photografting polymerization, only monodisperse nanoparticles, 30 nm in size, were grafted onto the substrate surface after photografting (Route 4) [139]. The formation mechanism of the particle includes the process of surface initiating, grafting combined with cross-linking, reversible termination and shish kebab growing. At first, the active chain radicals at the surface of the substrate initiated monomer to generate graft propagating chains. With the growing of the graft chains the emulsifier molecules are induced to surround the chains to form precursory particles. Meanwhile the cross-linker monomer DVB or MBA induces cross-linking among those chains to form the 3-D networks (the cross-linked growing

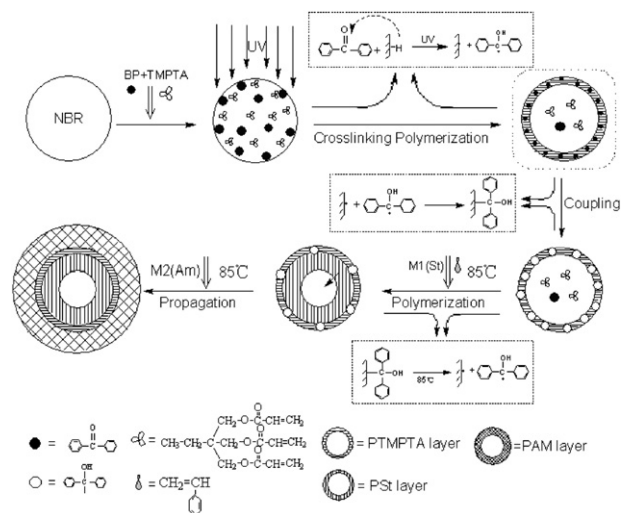
particles). Under the UV irradiation, the dormant groups onto the surface of the precursory particles can be reactivated to initiate the graft polymerization again (the feature of living grafting polymerization). With the helps of the emulsifier and the cross-linking monomers, new particles are formed on the former ones and result in the formation of the multilayered particles at last.

In summary, photografting polymerization is one of the most robust and facile tools to construct 3-D nanometer polymer particles with various topologies on polymeric substrates.

### 3.3. Photo-assisted fabrication of functional polymer particles

Generally, polymer particles with core–shell structures can be prepared by seeded emulsion polymerization, self-assembly of block copolymers with selective solvents, self-assembly of polymer chains on a core surface, layer-by-layer deposition and polymerization of monomers absorbed on a core surface. An alternative method for achieving a well-defined core–shell morphology is to graft polymer brushes through the use of initiators tethered chemically to the particle surface [30,142–149]. As mentioned above, the photo-induced grafting polymerization is not only applicable to planar surfaces, which can be directly exposed to the UV irradiation, but also to monoliths. Based on these achievements, Yang et al. [150,151] exploited the possibility of using a 2-step process to prepare core–shell polymer particles. The dormant groups were immobilized by a photo process and reactivated by a thermo-process. Commercially available vulcanized acrylonitrile butadiene rubber (NBR) latex was taken as the substrate and the pathway is depicted in Scheme 9.

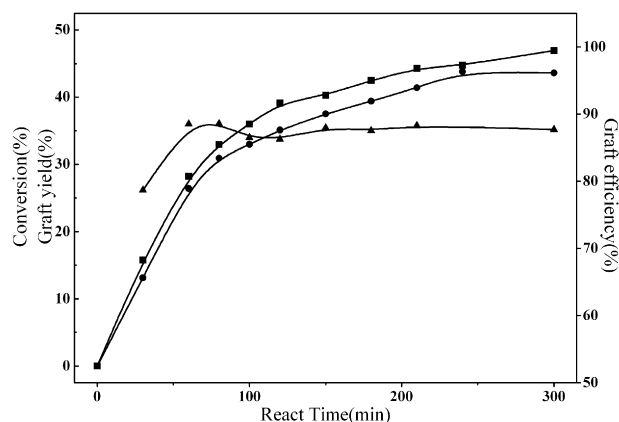
The immobilization of the dormant species onto the spherical particles by a photo process consisted in three steps: (1) BP and a small amount of the three-functional monomer trimethylpropane triacrylate (TMPTA) were dissolved in the NBR latex; (2) under UV radiation, a free radical surface/subsurface cross-linking polymerization was initiated by the BP photoreduction; (3) as a result of the cross-linking polymerization and the free radical coupling reaction with the semipinacol radicals, particles with large amounts of



**Scheme 9.** The schematic procedure and chemistry for a grafting polymerization on the surface of NBR latex particles. Reprinted with permission from Ref. [151]. Copyright [2007] Elsevier.

dormant semipinacol groups were obtained. The cross-linking reaction of TMPTA should favor an increase in surface coupling of the semipinacol groups. Subsequently, the particles with bonded dormant species were used to initiate the grafting polymerization *via* heating as shown in Fig. 10. A high grafting efficiency of approximate 90% was achieved. This demonstrated that the amount of homopolymers could be dramatically reduced due to the very low initiation reactivity of the semipinacol radicals produced by decomposition of NBR-SP at 85 °C in the heterogeneous polymerization system.

Interestingly, there were two grafting chain growing modes that depended on the nature of the monomers. Hydrophobic monomers, such as styrene, grafted from the particle surface and inwards in the particles. On the other hand, the hydrophilic monomers, such as acrylamide (AM), grew outwards from the particles surface. Fig. 11 presents TEM micrographs of NBR latex grafted with various monomers. The advantages of this technology are the high grafting efficiency, i.e., approx. 90%, and the fact that the grafting yields increased with time. The chain growth with a semipinacol free radical as the persistent radical demonstrated living polymerization features. Therefore, with subsequent addition of AM or NVP as



**Fig. 10.** Relationships between reaction time and monomer conversion (■), grafting yield (●) and grafting efficiency (▲). Experimental conditions:  $C_{\text{NBR}}$  23.7 wt%,  $C_{\text{St}}$  23.7 wt%, at 85 °C. Reprinted with permission from Ref. [151]. Copyright [2007] Elsevier.

a second monomer, a composite core–shell particle could be prepared. When the grafting yield was controlled at about 50%, the strength of the modified rubbers increased significantly without loss of elongation. It was demonstrated that the UV-screening effect of a latex particle is negligible and that photo-induced grafting polymerization can be applied to provide the polymer particles with a desired functionality.

Recently, photo-induced particle surface grafting polymerization has also been used to prepare Janus particles [152]. The technology involves particle assembly and immobilization steps, followed by a photo-induced grafting polymerization process. Typical images of Janus particles prepared by this technique are displayed in Fig. 12. In summary, this “grafting from” technique provides an opportunity to achieve stable layers of densely grafted polymers with a variety of compositions and functionalities on the surfaces of micro/nanoparticles such as latexes, gold, silica, etc.

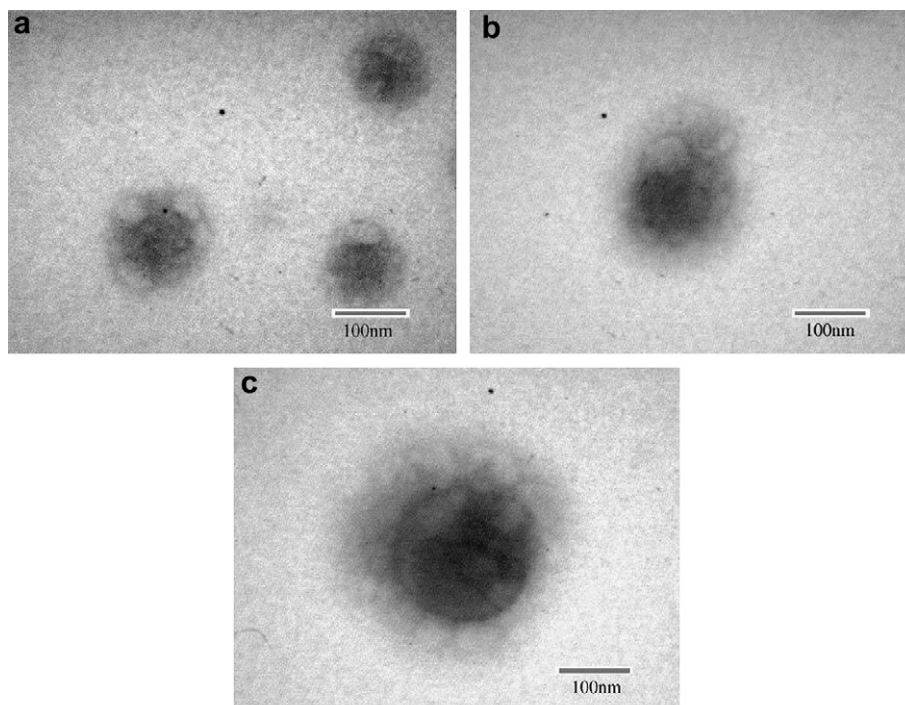
Most recently, photo-induced living polymerization has been successfully exploited in preparing ultrafine nano-sized hairy particles (20–35 nm) with soft hydrogel nanocores and PNIPAm as responsive hairs [153]. The preparation strategy is illustrated in Scheme 10. A cross-linked PAM nanocore (CLPAM) with a surface of semipinacol dormants was first prepared under UV radiation in an inverse microemulsion system with BP and a tertiary amine as the binary photoinitiator. Subsequently, the obtained CLPAM was dispersed in an aqueous medium containing the monomer *N*-isopropylacrylamide (NIPAm) to form PNIPAm hairs covalently bonded to the core surface. The particle size, morphology and especially the temperature-induced association and dissociation of these CLPAM@PNIPAm particles in aqueous solutions were examined.

#### 4. Summary and perspective

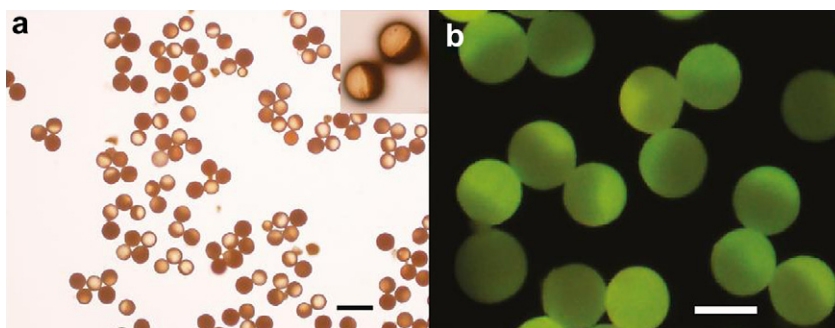
The photoinitiators, such as benzophenone, xanthone, acetophenone and 9-fluorenone, etc, can abstract a hydrogen atom from the C–H bond to form a polymeric free radical and the free radical of the photoinitiator derivative which functions as a stable/persistent free radical. There are two competitive reactions between the polymeric and the stable radicals. One is the initiation reaction in the presence of monomers, and the other is the termination reaction by coupling of two free radicals. Based on this fundamental chemistry, 1-step and 2-step photografting polymerization technologies have been developed. It has been demonstrated that the grafting polymerization has living polymerization features.

Many applications of photo-induced living polymerization have been described, such as modifying the surface properties of the polymeric films and sheets, enhancing the adhesion and lamination, offering the membranes with environment-stimulus properties, etc. Besides these conventional applications of polymer surface modification, the photo-induced grafting polymerization also has been exploited in modifying the surface of micro devices and non-planar substrates, for example, in nano and micro-polymer granules, in fabricating mono- and multi-layers of polymer particles onto the substrate and in assembling polymer particles strung by polymer chains. It should be highlighted that the technique allows the incorporation of a broad range of surface chemistry at specific and precisely defined locations of complicated profiles of the substrates with a photomask which cannot be realized with other grafting technologies. In addition to the grafting application, the photo-induced polymerization is also utilized to prepare polyacrylamide hydrogels with gradient cross-linking degrees [154].

However, there still remain challenges of photo-induced living polymerization in preparing polymers with well-defined structures, similar to those of other living free radical polymerization technologies, such as ATRP, RAFT and transitional metal mediated



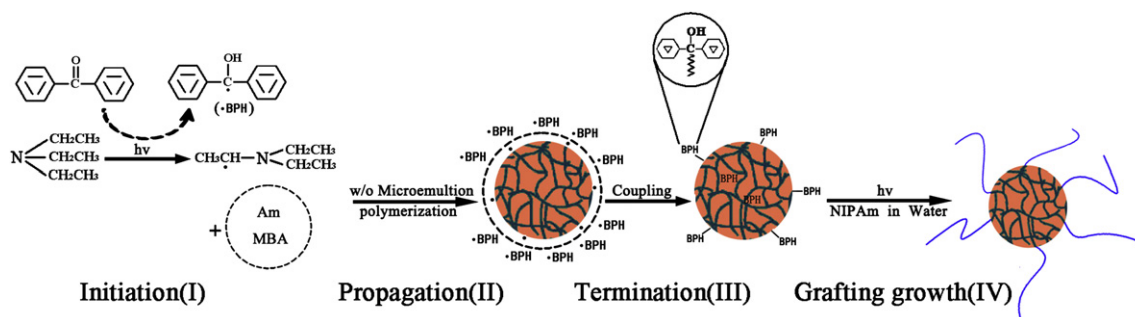
**Fig. 11.** TEM micrographs of (a) NBR/PSt, (b) NBR-g-PSt/PAm and (c) NBR-g-PSt/PVP. Conditions: CNBR/PSt 5.7 wt% (grafted for 2 h GY 42%),  $C_{AM}$  7.1 wt% in (b);  $C_{NVP}$  7.1 wt% in (c), grafted at 85 °C for 3 h. Reprinted with permission from Ref. [151]. Copyright [2007] Elsevier.



**Fig. 12.** Bicolor Janus particles after selective modification with PAM: (a) optical micrograph; (b) fluorescent micrograph of particles with diameters of 70 μm. The scale bars of images a and b correspond to 140 and 70 μm, respectively. Reprinted with permission from Ref. [152]. Copyright [2009] American Chemical Society.

free radical polymerizations. A possible explanation for this is that there are still irreversible terminations by coupling of polymer chains. In surface living grafting polymerization, one end of the polymer chains is tethered to the substrates. Despite these

challenges, photo-induced living polymerization still offers a novel chemistry and facile technology for fabricating linear grafted polymer brushes, branched polymer brushes, mono- and multi-layer polymer particles on flat and non-planar surfaces. So far, the



**Scheme 10.** A schematic of the procedure for a photo-initiated graft polymerization of a cross-linked PAM hydrogel coupled with BPH groups and hairy PNIPAm chains. Reprinted with permission from Ref. [152]. Copyright [2010] American Chemical Society.

published investigations have demonstrated its promising applications in preparing biomaterials, separation materials, optical and electromaterials.

An alternative option when it comes to solving the limitations of photo-induced living polymerization is to combine the photo-polymerization with other free radical living polymerization systems and to develop a new photocontrolled living polymerization system. There exist some emerging technologies and efforts in this regard. For example, studies include UV-stimulated RAFT polymerization [155,156], a living polymerization that involves photoexcited monomers [157], as well as organotellurium-mediated controlled/living radical polymerization initiated by direct C–Te bond photolysis [158].

## Acknowledgment

Financial support by Changjiang Scholars and Innovative Research Team in University (IRT 0706), the Programme of Introducing Talents of Discipline to Universities (B08003) and the National Science Foundation of China (No. 21074006) is gratefully acknowledged.

## References

- [1] Szwarc M. *Nature* 1956;178:1168–9.
- [2] Holden G, Milkovich R. Rubberlike block polymers. U.S. patent 3,265,765, 1966.
- [3] Khanna SN, Levy M, Szwarc M. *Trans Faraday Soc* 1962;58:747–7461.
- [4] Matyjaszewski K, Kubisa P, Penczek S. *J Polym Sci Part A Polym Chem* 1974; 12:1333–6.
- [5] Faust R, Kennedy JP. *J Polym Sci Part A Polym Chem* 1986;24:1874–96.
- [6] Jagur-Grodzinski J. Living and controlled polymerization: synthesis, characterization and properties of the respective polymers and copolymers. New York: Nova Science Publishers, Inc.; 2006.
- [7] 50 Years of living polymerization. In: Matyjaszewski K, Mueller AHE, editors. *Prog Polym Soc*, vol. 32; 2007. p. 1–282.
- [8] Kennedy JP, Ivan B. Designed polymers by carbocationic macromolecular engineering, theory and practice. Munich: Hanser; 1992.
- [9] Hsieh HL, Quirk RP. Anionic polymerization, principles and practical applications. New York: Marcel Dekker Inc.; 1996. p. 744.
- [10] Matyjaszewski K. Macromolecular engineering: from rational design through precise macromolecular synthesis and processing to targeted macroscopic properties. *Prog Polym Sci* 2005;30:858–75.
- [11] Matyjaszewski K, Xia J. *Chem Rev* 2001;101:2921–90.
- [12] Braunecher WA, Matyjaszewski K. *Prog Polym Sci* 2007;32:93–146.
- [13] Levy M. *Polym Adv Technol* 2007;18:681–4.
- [14] Moad G, Solomon DH. The chemistry of radical polymerization. 2nd ed. Oxford UK: Elsevier; 2006. 1–9.
- [15] Greszta D, Mardare D, Matyjaszewski K. *Macromolecules* 1994;27:638–44.
- [16] Goto A, Fukuda T. *Prog Polym Sci* 2004;29:329–85.
- [17] Bachmann WE, Wiselogle FY. *J Org Chem* 1936;1:354–82.
- [18] Perkins MJ. *J Chem Soc*; 1964:5932–5.
- [19] Otsu T, Yoshida M. *Makromol Chem Rapid Commun* 1982;3:127–32.
- [20] Otsu T, Yoshida M. *Makromol Chem Rapid Commun* 1982;3:133–40.
- [21] Otsu TJ. *Polym Sci Part A Polym Chem* 2000;38:2121–36.
- [22] Otsu T, Ogawa T, Yamamoto T. *Macromolecules* 1986;19:2087–9.
- [23] Higashi J, Nakayama Y, Marchant RE, Matsuda T. *Langmuir* 1999;15:2080–8.
- [24] Nakayama Y, Matsuda T. *Macromolecules* 1996;29:8622–30.
- [25] Lee HJ, Nakayama Y, Matsuda T. *Macromolecules* 1999;32:6989–95.
- [26] Kidoaki S, Nakayama Y, Matsuda T. *Langmuir* 2001;17:1080–7.
- [27] Kidoaki S, Ohya S, Nakayama Y, Matsuda T. *Langmuir* 2001;17:2402–7.
- [28] Matsuda T, Kaneko M. *Ge SR. Biomaterials* 2003;24:4507–15.
- [29] Matsuda T, Ohya S. *Langmuir* 2005;21:9660–5.
- [30] de Boer B, Simon HK, Werts MPL, van der Vegte EW, Hadziioannou G. *Macromolecules* 2000;33:349–56.
- [31] Benetti EM, Zapotoczny S, Vancso GJ. *Adv Mater* 2007;19:268–71.
- [32] Navarro M, Benetti EM, Zapotoczny S, Planell JA, Vancso GJ. *Langmuir* 2008; 24:10996–111002.
- [33] Benetti EM, Reimhult E, de Bruin J, Zapotoczny S, Textor M, Vancso GJ. *Macromolecules* 2009;42:1640–7.
- [34] Solomon DH, Rizzardo E, Cacioli P. U.S. patent 4,581,429, March 27, 1985.
- [35] Georges MK, Veregin RPN, Kazmaier PM, Hamer GK. *Macromolecules* 1993; 26:2987–8.
- [36] Kato M, Kamogato M, Sawamoto M, Higashimura T. *Macromolecules* 1995; 28:1721–3.
- [37] Wang JS, Matyjaszewski K. *J Am Chem Soc* 1995;117:5614–5.
- [38] Percec V, Barboiu B. *Macromolecules* 1995;28:7970–2.
- [39] Chiefari J, Chong K, Ercole F, Krstina J, Jeffery J, Le TPT, et al. *Macromolecules* 1998;31:5559–62.
- [40] Le TP, Moad G, Rizzardo E, Thang SH. *PCT Int Appl WO* 9801478 A1 19980115, 1998.
- [41] Satoh K, Kamigaito M. *Chem Rev* 2009;109:5120–56.
- [42] Tsarevsky NV, Matyjaszewski K. *Chem Rev* 2007;107:2270–99.
- [43] Oh JK, Bencherif SA, Matyjaszewski K. *Polymer* 2009;50:4407–23.
- [44] Pintauer T, Matyjaszewski K. *Chem Soc Rev* 2008;37:1087–97.
- [45] Ouchi M, Terashima T, Sawamoto M. *Acc Chem Res* 2008;41(9):1120–32.
- [46] Ouchi M, Terashima T, Sawamoto M. *Chem Rev* 2009;109:4963–5050.
- [47] Lowe AB, McCormick CL. *Prog Polym Sci* 2007;32:283–351.
- [48] Moad G, Rizzardo E, Thang SH. *Acc Chem Res* 2008;41(9):1133–42.
- [49] Moad G, Rizzardo E, Thang SH. *Polymer* 2008;49:1079–131.
- [50] Boyer C, Bulmus V, Davis TP, Ladmira V, Liu J, Perrier S. *Chem Rev* 2009;109: 5402–36.
- [51] Yang W, Rånby B. *Macromolecules* 1996;29:3308–10.
- [52] Kyomoto M, Ishihara K. *ACS Appl Mater Interfaces* 2009;1(3):537–42.
- [53] Kyomoto M, Moro T, Takatori Y, Kawaguchi H, Nakamura K, Ishihara K. *Biomaterials* 2010;31:1017–24.
- [54] Meng H, Liu L, Yang W. *J Macromol Sci Part A Appl Pure Chem* 2009;46: 921–7.
- [55] Bai H, Huang Z, Yang W. *J Polym Sci Part A Polym Chem Ed* 2009;47: 6852–62.
- [56] Yang W, Rånby B. *Euro Polym J* 1999;35:1557–68.
- [57] Ma H, Davis RH, Bowman CN. *Macromolecules* 2000;33:331–5.
- [58] Stachowiak TB, Svec F, Fréchet JMJ. *Chem Mater* 2006;18:5950–7.
- [59] Ma H, Davis RH, Bowman CN. *Polymer* 2001;42:8333–8.
- [60] Mikulasova D, Chrastova V, Crrovcy P, Horie K. *Makromol Chem* 1974; 178(2):429–42.
- [61] Li Y, Desimone JM, Poon CD, Samulski E. *J Appl Polym Sci* 1997;64:883–9.
- [62] Yang W, Rånby B. *J Appl Polym Sci* 1996;62:545–55.
- [63] Barbey R, Lavanant L, Paripovic D, Schuwer N, Sugnaux C, Tugulu S, et al. *Chem Rev* 2009;109:5437–527.
- [64] Ma Z, Gao C, Yuan J, Ji J, Gong Y, Shen J. *J Appl Polym Sci* 2002;85:2163–71.
- [65] Janorkar AV, Proulx SE, Metters AT, Hirt DE. *J Polym Sci Part A Polym Chem* 2006;44:6534–43.
- [66] Zhao B, Neoh KG, Liu FT, Kang ET. *Langmuir* 1999;15:8259–64.
- [67] Zhang J, Khong KT, Kang ET. *J Appl Polym Sci* 2000;78:1366–73.
- [68] Zhou X, Liu P. *J Appl Polym Sci* 2003;90:3617–24.
- [69] Castell P, Wouters M, Fischer H, With G. *J Appl Polym Sci* 2007;106:3348–58.
- [70] Zeiler T, Kellermann S, Munstedt H. *J Adhes Sci Technol* 2000;14:619–34.
- [71] Wang HL. *J Adhes* 2006;82:731–45.
- [72] Kang ET, Shi JL, Neoh KG, Tang KL, Liaw DJ. *J Polym Sci Part A Polym Chem* 1998;36:3107–14.
- [73] Kang ET, Neoh KG, Shi JL, Tan KL, Liaw DJ. *Polym Adv Technol* 1999;10:20–9.
- [74] Ei Kholdi O, Lecamp L, Lebaudy P, Bunel C. *J Appl Polym Sci* 2004;92: 2803–11.
- [75] Lei J, Gao J, Jiang L. *J Appl Polym Sci* 2006;100:2549–53.
- [76] Zhang J, Kato K, Uyama Y, Ikada Y. *J Polym Sci Part A Polym Chem* 1995;33: 2629–38.
- [77] Castell P, Wouters M, de With G, Fischer H, Huijs F. *J Appl Polym Sci* 2004;92: 2341–50.
- [78] Yamada K, Takeda S, Hirata M. *J Appl Polym Sci* 2007;103:493–500.
- [79] Yamada K, Kimura J, Hirata M. *J Appl Polym Sci* 2003;87:2244–52.
- [80] Yang Q, Hu M-X, Dai Z-W, Tian J, Xu Z-K. *Langmuir* 2006;22:9345–9.
- [81] Yang Q, Xi Z-K, Hu M-X, Li J-J, Wu J. *Langmuir* 2005;21:10717–23.
- [82] Yang Q, Tian J, Hu M-X, Xu Z-K. *Langmuir* 2007;23:6684–90.
- [83] Akbari A, Desclaux S, Rouch JC, Aptel P, Remigy JC. *J Membr Sci* 2006;286: 342–50.
- [84] Akbari A, Desclaux S, Rouch JC, Remigy JC. *J Membr Sci* 2007;297:243–52.
- [85] Asano M, Chen J, Maekawa Y, Sakamura T, Kubota H, Yoshida M. *J Polym Sci Part A Polym Chem* 2007;45:2624–37.
- [86] Chen J, Asano M, Maekawa Y, Sakamura T, Kubota H, Yoshida M. *J Membr Sci* 2006;283:373–9.
- [87] Taniguchi M, Kilduff JE, Belfort G. *J Membr Sci* 2003;222:59–70.
- [88] Kilduff JE, Mattaraj S, Pieracci JP, Belfort G. *Desalination* 2000;132:133–42.
- [89] Taniguchi M, Belfort G. *J Membr Sci* 2004;231:147–57.
- [90] Susanto H, Balakrishnan M, Ulbricht M. *J Membr Sci* 2007;288:157–67.
- [91] Kang JS, Lee SJ, Huh H, Shim JK, Lee YM. *J Appl Polym Sci* 2003;88:3188–95.
- [92] Hilal N, Al-Khatib L, Atkin BP, Kochkodan V, Potapchenko N. *Desalination* 2003;158:65–72.
- [93] Yang JM, Wang MC, Hsu YG, Chang CH. *J Membr Sci* 1997;128:133–340.
- [94] Wang HY, Kobayashi T, Fujii N. *J Chem Tech Biotechnol* 1997;70:355–62.
- [95] Piletsky SA, Matuschewski H, Schedler U, Wilpert A, Piletska EV, Thiele TA, et al. *Macromolecules* 2000;33:3092–8.
- [96] Sergeeva TA, Matuschewski H, Piletsky SA, Bendig J, Schedler U, Ulbricht M. *J Chromatogr A* 2001;907:89–99.
- [97] Ulbricht M. *React Funct Polym* 1996;31:165–77.
- [98] Kaeselev B, Kingshott P, Jonsson G. *Desalination* 2002;146:265–71.
- [99] Qiu C, Xu F, Nguyen QT, Ping Z. *J Membr Sci* 2005;255:107–15.
- [100] Yang B, Yang W. *J Macromol Sci Part A-Pure Appl Chem* 2003;A40:309–20.
- [101] Yang B, Yang W. *J Membr Sci* 2005;258:133–9.
- [102] Salam A, Ulbricht M. *Macromol Mater Eng* 2007;292:310–8.
- [103] Wang WC, Neoh KG, Kang ET, Lim SL, Yuan D. *J Colloid Interface Sci* 2004; 279:391–8.

- [104] Yeon K-H, Song J-H, Kim J-B, Moon S-H. *J Chem Technol Biotechnol* 2004;79:1395–404.
- [105] Zhong W, Yang Y, Yang W. *Thin Solid Films* 2005;479:24–30.
- [106] Shearer AEH, Paik JS, Hoover DG, Haynie SL, Kelley MJ. *Biotechnol Bioeng* 2000;67:141–6.
- [107] Yang W, Rånby B. *J Appl Polym Sci* 1997;63:1723–32.
- [108] Rånby B. *Int J Adh Adhes* 1999;19:337–43.
- [109] Rånby B. *Mater Res Innov* 1998;2:64–71.
- [110] Rånby B, Yang W. *Chin J Polym Sci* 2001;19:123–7.
- [111] Rohr T, Hilder EF, Donovan JJ, Svec F, Fréchet MJM. *Macromolecules* 2003;36:1677–84.
- [112] Wang T, Kang ET, Neoh KG. *Langmuir* 1998;14:921–7.
- [113] Wang H, Brown HR. *J Appl Polym Sci* 2005;97:1097–106.
- [114] Yang W, Rånby B. *J Appl Polym Sci* 1996;62:533–43.
- [115] Moro T, Takatori Y, Ishihara K, Konno T, Takigawa Y, Matsushita T, et al. *Nat Mater* 2004;3:829–37.
- [116] Moro T, Takatori Y, Ishihara K, Nakamura K, Kawaguchi H. *Clin Orthop Relat Res* 2006;453:58–63.
- [117] Kyomoto M, Moro T, Konno T, Takadama H, Kawaguchi H, Takatori Y, et al. *J Mater Sci Mater Med* 2007;18:1809–15.
- [118] Kyomoto M, Iwasaki Y, Moro T, Konno T, Miyaji F, Kawaguchi H, et al. *Biomaterials* 2007;28:3121–30.
- [119] Kyomoto M, Moro T, Miyaji F, Hashimoto M, Kawaguchi H, Takatori Y, et al. *J Biomed Mater Res Part A* 2009;90:362–71.
- [120] Kyomoto M, Moro T, Saiga K, Miyaji F, Kawaguchi H, Takatori Y, et al. *Biomaterials* 2010;31:658–68.
- [121] Kyomoto M, Moro T, Iwasaki Y, Miyaji F, Kawaguchi H, Takatori Y, et al. *J Biomed Mater Res Part A* 2009;91:730–41.
- [122] Moro T, Kawaguchi H, Ishihara K, Kyomoto M, Karita T, Ito H, et al. *Biomaterials* 2009;30:2995–3001.
- [123] Kato K, Uchida E, Kang ET, Uyama Y, Ikada Y. *Prog Polym Sci* 2003;28:209–59.
- [124] Goddard JM, Hotchkiss JH. *Prog Polym Sci* 2007;32:698–725.
- [125] Uyama Y, Kato K, Ikada Y. *Adv Polym Sci* 1998;137:1–39.
- [126] Bhattacharya A, Misra BN. *Prog Polym Sci* 2004;29:767–814.
- [127] Deng J, Wang L, Liu L, Yang W. *Prog Polym Sci* 2009;34:156–93.
- [128] Tang S, Xie J, Huang Z, Xu FJ, Yang W. *Langmuir* 2010;26(12):9905–10.
- [129] Nonaka T, Hashimoto K, Kurihara S. *J Appl Polym Sci* 1997;66(2):209–16.
- [130] Yang B, Yang W. *J Membr Sci* 2003;218:247–55.
- [131] Kyomoto M, Moro T, Konno T, Takadama H, Yamawaki N, Kawaguchi H, et al. *J Biomed Mater Res A* 2007;82:10–7.
- [132] Kyomoto M, Moro T, Miyaji F, Hashimoto M, Kawaguchi H, Takatori Y, et al. *J Biomed Mater Res A* 2008;82:439–47.
- [133] Goda T, Konno T, Takai M, Moro T, Ishihara K. *Biomaterials* 2006;27:5151–60.
- [134] Goda T, Konno T, Takai M, Ishihara K. *Colloids Surf B Biointerfaces* 2007;54:67–73.
- [135] Wang H, Brown HR. *Polymer* 2007;48:477–87.
- [136] Uchida E, Ikada Y. *Macromolecules* 1997;30:5464–9.
- [137] Wang Y, Yang W. *Langmuir* 2004;20:6225–31.
- [138] Wang Y, Zhong W, Jiang N, Yang W. *Macromol Rapid Commun* 2005;26:87–92.
- [139] Wang Y, Deng J, Zhong W, Kong L, Yang W. *Macromol Rapid Commun* 2005;26:1788–93.
- [140] Wang Y, Bai Y, Zhong W, Huang W, Yang W. *Macromolecules* 2007;40:756–9.
- [141] Wang Y, Qiu Z, Yang W. *Macromol Rapid Commun* 2006;27:284–8.
- [142] O'Reilly RK, Joralemon MJ, Hawker CJ, Woolley KL. *J Polym Sci Part A Polym Chem* 2006;44:5203–17.
- [143] Husemann M, Mecerreyes D, Hawker CJ, Hedrick JL, Shah R, Abbott NL. *Angew Chem. Int. Ed* 1999;38:647–9.
- [144] Prucker O, Rühle J. *Adv Mater* 1998;10:1073–7.
- [145] Quirk RP, Mathers RT, Cregger T, Foster MD. *Macromolecules* 2002;35:9964–74.
- [146] Zhao B, Brittain WJ. *Macromolecules* 2000;33:342–8.
- [147] Kong X, Kawai T, Abe J, Iyoda T. *Macromolecules* 2001;34:1837–44.
- [148] Husseman M, Malmstrom EE, McNamara M, Mate M, Mecerreyes D, Benoit DG, et al. *Macromolecules* 1999;32:1424–31.
- [149] Yu WH, Kang ET, Neoh KG. *Langmuir* 2005;21:450–6.
- [150] Wang Q, Liu L, Yang W. *Polym J* 2008;40:192–7.
- [151] Wang Q, Liu L, Yang W. *Polymer* 2007;48:6581–8.
- [152] Liu L, Ren M, Yang W. *Langmuir* 2009;25(18):11048–53.
- [153] Lv S, Liu L, Yang W. *Langmuir* 2010;26(3):2076–82.
- [154] Li S, Yang W. *Polym Adv Technol*, doi:10.1002/pat.1623.
- [155] Lu L, Yang N, Cai Y. *Chem Commun*; 2005:5287–8.
- [156] Lu L, Zhang H, Yang N, Cai Y. *Macromolecules* 2006;39:3770–6.

- [157] Tanabe M, Vandemeulen GWM, Chan WY, Cyr PW, Vanderak L, Rider DA, et al. *Nat Mater* 2006;5:467–70.
- [158] Yamago S, Ukai Y, Matsumoto A, Nakamura Y. *J Am Chem Soc* 2009;131:2100–1.



**Yuhong Ma** received his B.S. in 1987 and M.S. in 1990 majored in Polymer Science from Beijing Institute of Chemical Technology (BICT). After completing his M.S. study, he joined the department of polymer science of BICT as an assistant professor and earned his Ph.D. from Beijing University of Chemical Technology in 2003 under the guidance of Prof. Wantai Yang. From July 2004 through March 2008, he had been worked in Kemet Electronics (Suzhou) Co. Ltd as Manager of Development Engineering (China). Since June 2008, he has been at Beijing University of Chemical Technology as an associate professor. His research interests include photo-induced living free radical polymerization, inorganic/organic composite films, and grafting polymerization of polyolefins.



**Lianying Liu** received her Ph.D. degree in College of Materials Science and Engineering at Beijing University of Chemical Technology in 2003. Since then, she has been a member of the Organic Materials Surface Science and Engineering Lab headed by Prof. Wantai Yang. Her current research interests include the design of nano- or micro- particles with novel architectures.



**Wantai Yang** is currently the dean of the College of Material Science and Engineering at Beijing University of Chemical Technology (BUCT). He received his B.S. from Tsinghua University in 1982 and his M.S. from Beijing Institute of Chemical Technology (BICT) in 1985. After completing his M.S. study, he joined the department of polymer science of BICT as an assistant professor. From 1993 to 1996 he had been a visiting scholar in Royal Institute of Technology (Sweden), and earned his Ph.D. under guidance of Prof. Rånby Bent in 1996. Then he returned to BICT as a professor in department of polymer science. He was awarded an NSFC Outstanding Youth Fund in 2000 and Cheung Kong Scholars Professor in 2001. He has co-authored over 300 peer-viewed papers and 70 patents. His research interests include living free radical polymerization, surface chemistry of organic materials, and new resources for polymer chemistry.