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Polymer brushes Architecture on the modified surfaces

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ABSTRACT

In last few decades, extensive research has been performed designing new synthetic procedures not only to create new classes of polymers, but also to control the architecture of those polymers. In order to improve the biocompatibility of medical implants and control to improve their interactions with proteins, cells and bacteria, it is important to modify the surfaces with different types of molecules. Specific polymers are often the molecules of choice because their properties can be tuned such as enhancement of surface hydrophilicity. The polymer architecture plays an important role at resisting protein adsorption or enhancing cell behavioural responses by already adsorbed proteins. The aim of this study was to give an overview of polymer brushes to study their natures and behavior on the surfaces.

Introduction

Surface chemistry plays an important role effecting for example tribological features [1], where the surface modification technique include introduction of specific functional groups on a surface. Modification of the chemical composition of the surface by polymer brushes or specific functional groups has been found to be a more reliable technique to tailor the surface properties to be more applicable in different biomedical applications [2-4]. Self-assembled monolayers (SAMs) containing initiators have been used for polymerisation of different monomers from the surface to obtain polymer brushes. The generation of a polymer brush on the surface is where one end of a linear polymer is attached to the surface (Figure 1) , while the second end is free and can be a different functional group used for a variety of applications [5-7].

The behaviour of polymer brushes on the surfaces could be:

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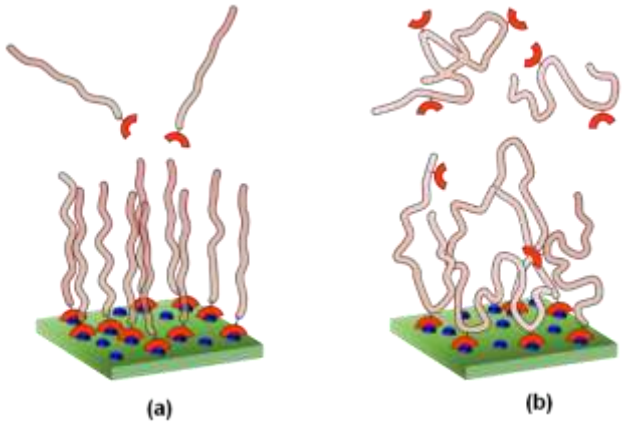

Figure 1. Polymer brush formation on surface via (a) terminal functional group, (b) side functional group

Homo-polymer brushes:

This type of polymer refers to those having one type of repeating unit in the backbone of the tethered polymer, and it can be divided into those being charged or neutral with the chains that comprise the polymer brush being rigid or flexible. The attached polymer appears as a ‘mushroom’ form when in good solvent, while in the presence of a poor solvent as the polymer has a ‘pancake’ structure, especially when the interaction with the solvent is weaker than with the substrate. If the solution can partially dissolve the

polymer the grafted chains interact with neighbours [8]. This interaction is either stretched away from the surface or in the formation of pinned micelles (clusters) in the presence of good and poor solvents respectively. Polymer brushes have been considered the main subject of many studies. For instance, the study done by Yeung, *et al*., demonstrated the effect of a poor solvent on a grafted homopolymers layer, using a combination of random phase approximation and numerical mean field calculations, and the result confirmed that the grafted polymer layer is unstable as the solvent quality decreases. That is, the interaction of polymer layer is stronger with the surface than with the solvent molecules [9]. Moreover, Grest *et al*. showed by molecular dynamic simulations the different behaviours of polymer brushes in good and poor solvents [10].

Random copolymer brushes:

These types of polymers contain two different repeating units randomly distributed along the polymer chain. For example, Mansky *et al*. poly styrene and methyl methacrylate by living radical polymerisation as random copolymer. These polymers after reaction with the initiator 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) were then attached through the hydroxyl (OH) and TEMPO end groups to the silicon wafer to produce brushes on the surface which known as polymer brushes [11]. In recent years, studies have focused on polymer brushes containing two types of polymers (amphiphilic). Brushes of two polymers having different molecular weights and the same chemical structure were highlighted in theoretical [9, 12] and experimental studies [13]. Researchers have analysed the properties of copolymer brushes, and it has been found that the morphology of brushes is affected by the solvent quality.

Mixed polymer brushes:

It consist of more than one homopolymer chains and can be modified to achieve different features, such as adhesion, friction, biocompatibility, colloidal stability, and conductivity. By contrast, modification of the surface requires the adhesion of different materials that have hydrophobic or hydrophilic properties or allow for selective adsorption of certain species. As a result, the creation of a mixed polymer brush layer, by mixing two or more homopolymers with different functionality in one layer, where each component has a specific property, induces the modified surface to behave differently. This emphasizes the difference between randomly grafted homopolymer brushes with different functionalities and brushes composed of random copolymers with two or more monomer units with different functionalities [14]. Solvent quality has also shown to have an effect on polymer morphology. Soga *et al* studied the equilibrium structure of binary polymer brush in different solvent state [15].

Mixed polymer brushes have many applications, one of the most important application is antifouling. For example Fu *et al* prepared poly(*N*-hydroxyethyl acrylamide) (polyHEAA) by ATRP and cationic poly(trimethylamino) ethyl methacrylate chloride (polyMETAC) on silicon wafer by surface-initiated photoiniferter-mediated polymerisation (SI-PIMP) and they studied the antibacterial and antifouling propertied of mixed polymers [16].

Block-copolymer brushes:

Macromolecules can consist of linear or non-linear polymeric chains (blocks), and one or two polymer chains covalently connected to each other. Generally, blocks are incompatible materials, and lead to a variety of well-defined self-assembled structures in different solvents and are important in different applications, such as thermoplastic elastomers, photonic materials and drug delivery system (DDS). For this reason, there is a continuous examination of the self-assembly processes and the response of these materials to external stimuli. As a result, these materials play an important role in modern macromolecular science covering polymer chemistry, polymer physics, and its applications [17]. Zhao *et al*. [18] synthesised block copolymer brushes of polystyrene-block-poly(methyl methacrylate) monolayers on a silicate surface using atom transfer radical polymerisation (ATRP) and carbocationic techniques. Similarly, Matyjashewski *et al*. [19] synthesised block copolymers of styrene and acrylates on silicon wafers by ATRP.

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هندسة الفرش البوليمرية على السطوح المطورة

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الملخص:

في العقود القليلة الماضية، تم إجراء أبحاث مكثفة لتصميم إجراءات تركيبية جديدة ليس فقط لإنشاء فئات جديدة من البوليمرات، ولكن أيضًا للتحكم في بنية تلك البوليمرات. من أجل تحسين التوافق الحيوي للغرسات الطبية والتحكم في تحسين تفاعلاتها مع البروتينات والخلايا والبكتيريا، من المهم تعديل الأسطح بأنواع مختلفة من الجزيئات. غالبًا ما تكون البوليمرات المحددة هي الجزيئات المفضلة لأن خصائصها يمكن ضبطها مثل تعزيز قابلية السطح للماء. تلعب بنية البوليمر دورًا مهمًا في مقاومة امتصاص البروتين أو تعزيز الاستجابات السلوكية للخلايا بواسطة البروتينات الممتصة بالفعل. كان الهدف من هذه الدراسة إعطاء نظرة عامة على فرش البوليمر لدراسة طبيعتها وسلوكها على الأسطح

الكلماتٍ المفتاحٍت: الفرش البوليمرية ، البوليمرات سلوك الفرش البوليمرية.