Polymer brushes for antibiofouling and lubrication

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Abstract

Surface-initiated atom transfer radical polymerization (SI-ATRP) could provide many merits for the preparation of polymer brush, such as the well-defined chemical configurations, gradient, architecture and thickness. To date, SI-ATRP has been a popular strategy to tailor the physicochemical properties of material interfaces. In this short review, the recent progresses of our group and others' in preparing methodologies of polymer brushes through SI-ATRP are highlighted in detail, including the fundamental mechanistic and superior characteristics. Some novel SI-ATRP techniques which are trigged by external-stimuli and the preparation of micro/nanoscale polymer hierarchical architecture with tailorable chemical components are also emphasized. Besides, since the polymer brush with different chemical components (e.g., single-component and multi-components) and multi-scale structural characteristics shows great impact on the physicochemical properties at interface and polymer brush are generally sensitive to the external stimuli, the polymer chains modified surfaces acted as smart materials show great potential in many fields. The application advancements of polymer brush are reviewed mainly in two aspects, including antibiofouling and lubrication. Finally, the opportunities and challenges for further application are addressed.
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Keywords: Polymer brush; Surface-initiated atom transfer radical polymerization; Antibiofouling; Lubrication

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1. Introduction

1.1. Polymer brush

Generally, thin polymer film in which all of the polymer chains are anchored by one chain end to the substrate is defined as polymer brush [1]. Three typical polymer chain conformations can be observed with increasing the grafting density of polymer brush and its molecular weight as follows: from the so-called "pancake" and "mushroom" regime at low grafting densities to the high density "brush" regime (Fig. 1). The pancake configuration is attributed to the collapse and entanglement of spare polymer brushes and brush array is induced by the steric repellency among the dense polymer chains. Besides, the polymer brush would like to stretch away from the substrate due to combined effect of steric and osmotic repulsion in a suitable solvent and in a poor solvent, however, the polymer chains collapse because of enough interior free space. Since facile controllability of polymer brush physico-chemical properties in terms of components, surface morphology and surface charge, etc. It has been a promising strategy for surface modification. While, the reported polymer brush synthetic methods are still not completely oxygen friendly, thus large scale preparation, for example, the industrial scale, has been hindered.

1.2. The preparation of polymer brush

The polymer chains could be anchored to the surface either through covalent bonding or physical adsorption. In general, physical adsorption involves the noncovalent interactions such as hydrogen bond, hydrophobic interaction, and electrostatic interaction. These attach processes are always reversible and therefore suffer from external mediums, including solvation and fluid shear force, etc. However, different from that, two typical strategies are utilized for the covalent bonds immobilized polymer brush and described as "grafting to" and "grafting from" [2,3]. For the grafting to technology, the anchor of polymer chains is accomplished by the reactions of (end)-functionalized appendixes with surface functionalities. While, because of the steric repellency effects between polymer chains and unfavorable reaction direction, the grafting to method always suffers from some evitable limitations, such as low grafting densities and limited film thickness. In the case of grafting from strategy, different with the grafting to method which makes it difficult to tether long polymer chain ends at short intermolecular distance, grafting from method is a bottom up strategy in which the initiator is anchored on the surface firstly, and can prepare the polymer chains via surface-initiator polymerization (SIP). SIP allows precisely control over polymer brush thickness, composition and architecture, thus surface-initiated polymerization has become one of the most extensively utilized methods to tailor the physicochemical properties of surface/interface in the recent years [4–9]. In this way, grafting from approach allows access to higher grafting densities and shows great application potentials for surface modification. Especially, the emergence of living radical polymerization in 1982 [10] has rapidly promoted the revolution of SIP in terms of polymerization methodologies. Including surface-initiated atom transfer radical polymerization (SI-ATRP), [11] transition metal-catalyzed living radical polymerization, [12] single-electron transfer and single-electron transfer degenerative chain transfer living radical polymerization, [13] ring-opening metathesis polymerization (ROMP), [14] surface reversible addition-fragmentation chain transfer polymerization (S-RAFT), [15,16] surface-initiated nitroxide-mediated polymerization (SI-NMP), [17,18] etc. Because of mild reaction condition, simple experimental setup and compatibility with aqueous and organic media, these radical living polymerization techniques have been frequently applied in various surface/interface engineering. In particular, the rapidly development of ARTP has greatly facilitated the SIP techniques [3,5,19,20] and it is considered that the SI-ATRP is one of the most promising techniques for designing and preparing of functionalized smart surface/interface. A variety of polymer brushes have been prepared with varying composition and morphology using SI-ATRP strategy, such as homogeneous, patterned and gradient polymer brushes. However, further application of traditional SI-ATRP has been trapped inevitably by some limitations, including large consumption of monomers, restricted operation condition, limited controllability, and environmental issues.

Typically, bulk ATRP is conducted through a redox-active transition metal complex (most commonly a copper catalyst). As depicted in the Scheme 1, copper catalyst Cu(I)/L at lower oxidation state reacts with initiator (alkyl halides), living

Fig. 1. Schematic illustration of three typical configurations of surface attached polymers with increasing grafting densities.