Surface Grafted Polymer Brushes: Potential Applications in Textile Engineering

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Abstract: Polymer brushes are assemblies of macromolecules that are tethered by one end to a surface or interface. The advantage of polymer brushes over other surface modification methods (e.g. self-assembled monolayers) is their mechanical and chemical robustness, coupled with a high degree of synthetic flexibility towards the introduction of a variety of functional groups. In this paper, an overview of the representative synthesis method of polymer brushes is presented and their potential applications on smart surfaces, wettability and biocompatible surfaces are explored. Their potential applications in textile engineering are discussed.

Keywords: polymer brush, surface-initiated polymerization, bio-compatible surface, patterned brush, smart surface

1. Introduction

Polymer brushes are assemblies of macromolecules that are tethered by one end to a surface or interface [1, 2]. For solid surfaces, the polymer chains can be chemically bonded to the substrate or may be just adsorbed onto the surface. Physisorption on a solid surface is usually achieved by block copolymers with one block interacting strongly with substrate and another block interacting weakly. For interfaces, the attachment may be achieved by similar adsorption mechanisms in which one part of chain prefers one medium and the rest of chain prefers the other. Polymer brushes on almost any substrate can be divided into neutral polymer brushes and charged polymer (polyelectrolyte) brushes [3]. The advantage of polymer brushes over other surface modification methods [e.g. self-assembled monolayers (SAMs)] is their mechanical and chemical robustness, coupled with a high degree of synthetic flexibility towards the introduction of a variety of functional groups [4,5]. There is also an increasing interest of using functional or diblock copolymer brushes for "smart" or responsive surfaces, which can change property when subjected to an external environment, such as temperature, pH, solvent, or electrolyte [6-8]. The polymer brushes are widely used to tailor surface properties such as wettability, corrosion resistance, actuation and biocompatibility, and thus have potential applications in textile industry.

2. Synthesis of Polymer Brushes via Surface Grafted Strategies

Polymer brushes are typically prepared through either physisorption or covalent attachment. Of these synthetic methods, covalent attachment is preferred because it overcomes the constraints of physisorption, namely, thermal and solvolytic instability. Covalent attachment can be achieved through "grafting to" and "grafting from" method [9, 10]. "Grafting to" method requires the tethering of end-functionalized polymer chains grafted directly to a surface via a chemical reaction of the end-groups with complimentary groups on the grafting surface. However, this approach often suffers from low grafting density and film thickness because of the requirement that polymer molecules must diffuse through an existing attached polymer layer to reach the reactive sites on the surface. Thus, steric hindrance for surface attachment increases as the thickness of the polymer film increases.

As a result of these limitations, "grafting from" method has become the preferred option for the synthesis of polymer brushes [11]. This approach uses a surface-immobilized initiator and subsequent in situ polymerization to generate polymer brush [12]. This approach has been used to prepare thick polymer brushes that are covalently anchored to substrate with a higher grafting density. The major advantage of the "grafting from" approach is that the tightly tethered chains may be grown from the grafting surfaces. The active end-centers of the growing chains are easily accessible for monomer units when monomers swell the brush. Thus, the highest grafting density can be approached with the "grafting from" method.

The controlled radical polymerization seems to be the most technically simple method. The important step of "grafting from" (also called surface initiated polymerization) approach is immobilization of initiator for certain polymerization. Ideally, the polymerization is not only surface-initiated but also surface-confined. In order to achieve maximum control of brush density, polydispersity, composition, and at the same time allowing the formation of block copolymers on the surface, a controlled polymerization is highly desirable. Over the last few years, this field has rapidly evolved and all the major controlled polymerization strategies have been used to prepare polymer brushes.

Ring opening metathesis polymerization (ROMP) of cyclic monomers, in particular functionalized norbornenes, has recently attracted attention for useful electrical properties (Scheme 1). Coating conductive substrates with well-defined polymer brushes may be of great use in the production of polymer electronic devices [13]. Whitesides used an immobilized ruthenium catalyst to grow brushes from norbornene-derived monomers on silicon wafer surfaces. Some of the thickest films produced using surface-initiated polymerization was grown in short times using a surface- immobilized ruthenium catalyst [14]. Nitroxide-mediated polymerization (NMP) (Scheme 2), a living polymerization technique based on reversible capping of the active chain-end radical with a nitroxide leaving group, has been used to synthesize polymer brushes on substrates by Husseman et al. Using surface-bound alkoxyamine initiator molecules on silicon substrates, over 100

nm thick polystyrene brushes were obtained in 16 hours [15]. Reversible addition-fragmentation chain transfer (RAFT) polymerization as shown in Scheme 3 is a controlled polymerization in which monomer is initiated using a conventional method (for example by a free radical initiator such as Azo-bis-isobutryonitrile) and mediated by a dithioester chain transfer agent [16]. Although this polymerization is slow when compared to methods such as ATRP or NMP, it is highly living. This was demonstrated by the re-initiation of the polymer chains to grow block copolymer brushes of polystyrene-b-Poly [(2-(Dimethylamino) ethyl methacrylate)] and Poly [2-(Dimethylamino) ethyl methacrylate]-b-polymethacrylate. A linear increase in brush thickness with re-initiation reaction number shows that virtually no termination reactions are occurring during brush growth [17].
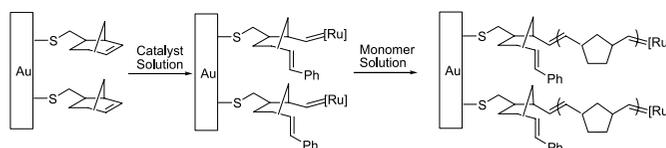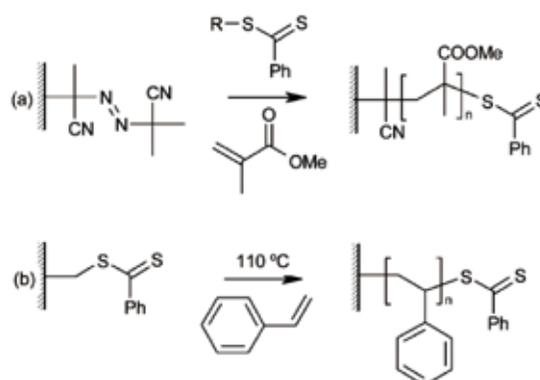

Scheme 1 Polymer brush grown by ROMP.
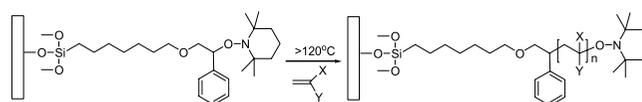
St: X=H,Y=C₆H₅; AAc: X=H, Y=COOH; HPMA:X=CH₃, Y=CONHCH₂(OH)CH₃; NIPAAm: X=H, Y=CONHCH(CH₃)₂

Scheme 2 Polymer brush grown by NMP and the mechanism of NMP.

Scheme 3 Mechanism of RAFT Polymerization and Polymer brushes grown by RAFT polymerization.

In recent years, atom transfer radical polymerization (ATRP) has been the most widely employed method for the preparation of polymer