Photoinitiated synthesis of polymer brush from dendritic photoinitiator electrostatic self-assembly†

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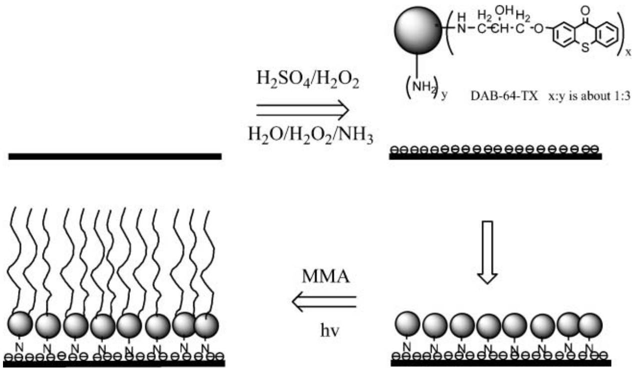
We report on a simple and effective method to prepare polymer brush by electrostatic self-assembly of dendritic macrophotoinitiator and photoinitiated polymerization.

Surfaces modified with thin polymer films have attracted attention[1,2] because of their potential application in many surface-based technologies such as biomaterials, adhesion and wetting, molecular recognition and microfluidics.[3–9] Polymer brushes, which can be prepared by chemical bond formation between reactive groups on the surface and reactive endgroups or by physisorption, have been widely used to tailor surface properties such as wettability and biocompatibility.[10] Compared with methods of physisorption and 'graft to', surface-initiated polymerization ('grafting from'), based on initiators bound to surfaces to initiate polymerization to generate tethered polymers, is a powerful alternative to control the thickness, functionality and density of polymer brushes with molecular precision.[10] Because of a tolerance for moisture and a wide variety of organic functional groups, radical polymerization is preferred for many applications.[11–16] Furthermore, photochemical initiation is a convenient way for the initiation of radicals and has some obvious advantages.[17–20] The self-assembly technique is the most important method for immobilization of photoinitiator on substrate surface.[1,10] In particular, electrostatic self-assembly is a very rapid and convenient way to fabricate the monolayer on the substrate.[21]

In this context, the dendritic photoinitiator is immobilized on the quartz slides by electrostatic self-assembly, then photoinitiated methylmethacrylate (MMA) to generate the polymer brush (Scheme 1). Through introducing an appropriate amount of thioxanthone moieties into the periphery of the water-soluble dendrimer of poly(propyleneimine) (PPI), water-soluble dendritic photoinitiator of DAB-64-TX was prepared.[22] This kind of functional dendrimer has a well-defined macromolecular structure with three-dimensional architectures, varied surface functionality, and many unique properties, and is the most promising candidate for self-assembly.[23] Because of the large amounts of amino group, the DAB-64-TX dendritic photoinitiator can be easily absorbed on to the anionic surface of the quartz slide by electrostatics in the aqueous solution. In the layer of DAB-64-TX, the photolysis of thioxanthone, in the presence of amines leads to the formation of a radical produced from a carbonyl compound (ketyl-type radical) and another radical derived from an amine. The amine radical usually initiates the polymerization of vinyl monomers to generate polymer brush.



Scheme 1

To explore the electrostatic self-assembly process of DAB-64-TX on the surface of the quartz slide and the process of generating the polymer brush, we monitored these processes by several measurements such as UV-vis spectrum, AFM, XPS and ellipsometry. Before any measurements, we washed the polymer brush thoroughly by Soxhlet extraction using toluene as solvent, in order to remove all of the unbound polymer formed in solution during photoinitiated polymerization. At the same time, the nonpolar toluene solvent does not destroy the layer of DAB-64-TX constructed by electrostatic self-assembly.

UV-vis absorption spectra of the self-assembly layer and polymer brush are shown in Fig. 1. The maximum absorption of the self-assembly layer is about 400 nm, which is the typical absorption of TX moieties in DAB-64-TX.[22] This shows that

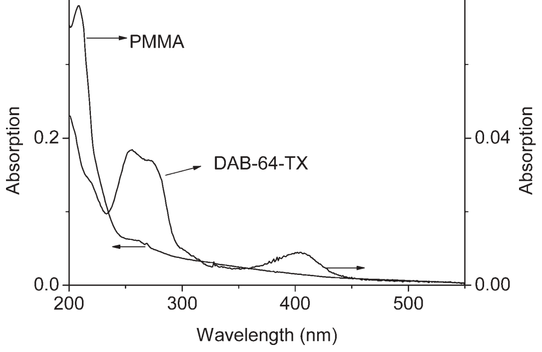


Fig. 1 UV-Vis absorption spectra of DAB-64-TX photoinitiator's layer and polymer brush layer on the quartz slide.

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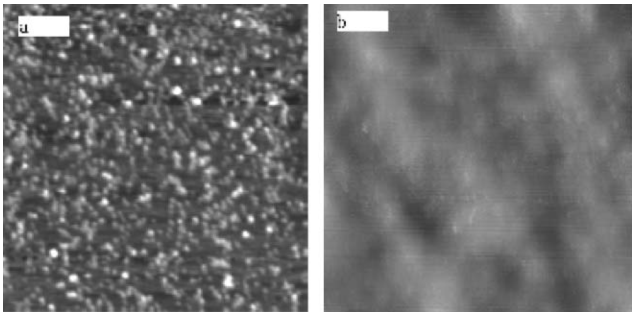

Fig. 2 Atomic force microscopy (AFM) images of DAB-64-TX photoinitiator's layer (a) and polymer brush layer (b). Scan size is 1 × 1 μm × 5 nm.

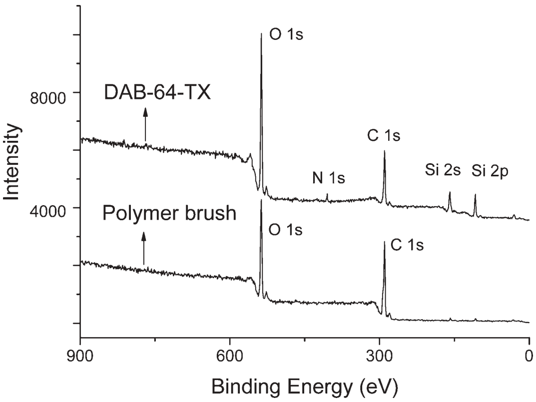

Fig. 3 XPS spectra of DAB-64-TX photoinitiator's layer and polymer brush layer on the quartz slide

DAB-64-TX dendritic photoinitiator is successfully self-assembled on the surface of a quartz slide, which can be confirmed further by AFM (see Fig. 2(a)). The average thickness of the DAB-64-TX layer is about 7 nm as measured by ellipsometry. From Fig. 2(a), the DAB-64-TX photoinitiator is immobilized and arrayed on the surface by strong electrostatic cohesion, to generate the photoinitiator's layer over the quartz slide's surface. This is very important for preparing the polymer brush. XPS measurements were also used to verify that the layer of DAB-64-TX attached to the surface. In Fig. 3(c), 1s (285 eV), and N 1s (401 eV) peaks indicate the existence of the photoinitiator's layer on the surface, which is in very good agreement with measurements of UV-vis absorption, AFM and ellipsometry. In the XPS spectrum, however, there are peaks of O 1s, Si 2s and Si 2p, which can be ascribed to the substrate of SiO_2 underneath. Fan[21] and Pruker[24] have obtained similar XPS results. Because the escape depth of the photoelectron (about 10 nm) is greater than the 7 nm thick DAB-64-TX layer, peaks about the SiO_2 substrate appear.

After photoinitiated polymerization, the typical strong absorption of PMMA appears at 208 nm in Fig. 1. This indicates the generation of polymer brush, whose thickness is about 100 nm as measured by ellipsometry. The Mn and polydispersity of PMMA from the bulk solution are 75 400 and 1.56, respectively, which are similar to those of grafted polymer.[17] Compared with the AFM picture of the DAB-64-TX photoinitiator's layer, the surface becomes very smooth and homogeneous (Fig. 2b), and is absent of DAB-64-TX particles. This shows that polymer brush provides full coverage over the surface, which can be further confirmed by an XPS spectrum of polymer brush. The presence of only peaks of O 1s and C 1s in the XPS spectrum (Fig. 3) indicates no exposure of DAB-64-TX layer or SiO_2 substrate.

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