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Substantially enhanced stability against degrafting of zwitterionic PMPC brushes by utilizing PGMA-linked initiators

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ABSTRACT

We present a simple method to prepare zwitterionic poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) brushes on silicon surfaces that exhibit excellent long term stability in aqueous environment. First, we attach poly(glycidyl methacrylate) (PGMA) to the substrate. Next, we couple 2-bromoisobutyryl bromide initiators to the modified substrate, which allows us to grow PMPC brushes using surface initiated atom transfer radical polymerization. Atomic force microscopy (AFM) is employed to evaluate the dry thickness of the PMPC brushes after incubation in water and solutions of various salts. The AFM results show that the PGMA-PMPC brushes are indeed very stable and that the brushes can stand being immersed for at least 4 weeks in physiological fluids (saline solution) and artificial sea water with only 1% decrease of their dry thickness. In view of potential applications, we demonstrate that the friction between these PGMA-PMPC brushes and a polystyrene colloid in water is extremely low: the friction coefficients are found to be 10^{-3}–10^{-4}. Moreover, we show that our brushes keep their hydrophilic properties after immersion for 100,000 ppm hours in sodium hypochlorite solution, indicating their potential for employment as coatings on industrial membranes.

1. Introduction

Triggered by the recent increase in the demand of functional surface coatings [1,2], there has been a quickly growing scientific interest in polymer brushes [3–8]. These brushes are dense films of macromolecules that are attached with one end to a surface. Surfaces decorated with brushes can be employed for controlling surface wettability [9,10], adhesion [4,11–13] and friction [14–17], and can be utilized in sensing [18,19] and drug delivery [20,21], among others. In particular, zwitterionic polymer brushes, which bear both cationic and anionic groups in the same polymer chain, have drawn considerable attention, due to their excellent performance as lubricants [22–24] and low-fouling coatings [25–27]. Moreover, they are often bio-compatible [28,29], which makes them potential candidates for applications that are used in the human body, for example on the interface of artificial joints [29,30] and on catheters [31].

A well-studied example of a zwitterionic polymer is poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC). Brushes composed of such polymers show extremely low sliding friction, which is even lower than typical values found in human synovial joints [22]. A possible reason for this low frictional response is that water molecules can cooperatively bind with the zwitterionic moieties in the brushes resulting in a strong hydration [32]. As a consequence, the osmotic pressure in the polymer brush system is high and, therefore, the effective contact area is low, *i.e.* friction is low during single asperity sliding. Therefore, these brushes hold great

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potential for employment in devices or machines where low friction is required. However, a critical disadvantage, which has prevented application of the brushes, is that the polymers can be cleaved off the surface when being immersed in aqueous solutions for several days [33–35].

The degrafting of PMPC brushes and other brushes is in most cases caused by hydrolysis, which can be tension-induced or -enhanced and results in breaking of the bonds between the polymer and the grafting surface [36–38]. Strongly hydrated polymer brushes such as PMPC where the osmotic pressure and the stretching is high [34] are particularly sensitive to cleavage due to a better access of water to the hydrolysis sensitive bonds, but also due to the potential mechano-chemical shift in the hydrolysis equilibrium. In acidic and alkaline solutions [39,40], the cleavage of particular bonds can be accelerated even more. Which bond will break depends on the type of surface in combination with the type of anchor or polymerization-initiator used to prepare the brushes [37,41–45]. It has been shown using molecular dynamics simulations that the highest tension occurs at the bond closest to the surface [46]. This bond is, therefore, often considered to be the most likely candidate for breakage. However, other bonds in the brush-anchors, such as the common ester or amide bonds, can be sensitive to hydrolysis too [41,47]. Besides hydrolysis, the degrafting also can be intentionally achieved by trace amounts of HF formed in the solvent, which can partly etch the silicon-oxide grafting-surface [43] or the utilization of light-sensitive linkers between the polymer and the surface [48,49].

In the last years, many methods have been developed to slow down degrafting of brushes from the surfaces [33,34,41,50–52]. Examples include the use of dense bottle-brushes where the backbone attaches to the surface [53] and the employment of long hydrophobic alkyl-chains that reduce hydrolytic activity by preventing water molecules from reaching the surface-bond [54]. Alternatively, self-healing polymer coatings can be used to counter-act brush degradation by the polymer-reattachment [50]. In this article, we build on these developments, as well as on our own expertise in this area [33,55]. In a recent article, we have for example shown that the degrafting of neutral, water-soluble brushes is significantly slowed down by utilizing trimethoxysilane-based instead of monochlorosilane-based surface-initiated atom transfer radical polymerization (SI-ATRP) initiators [55]. The former silane can bind to the surrounding silanes and the surface creating more anchor-points. Moreover, an amide bond in the trimethoxysilane replaces the ester-bond in the monochlorosilane. The latter bond is considered to be slightly more hydrolysis-sensitive (at extreme pH and temperature) than the amide [56]. The method of Ref. [55], however, only works for neutral polymers. For more hydrophilic, charged or zwitterionic polymers such as PMPC, the brushes still detach [33,34,57]. For such very hydrophilic polymers, diblock copolymers systems have been proposed to obtain stable surface-coatings [33,52,58]. Yet, under particular solvent conditions these coatings can phase-separate creating a rough, heterogeneous surface [33].

In this article, we present a simple method to fabricate homogeneous and robust PMPC brushes, which show a substantial enhanced stability against degrafting in water and salt solutions. To do so, we modify the poly (glycidyl methacrylate) (PGMA)-macro-initiator method first reported by Liu et al. [59], where bromoacetic acid (BAA) initiators or 2-bromo-2-methylpropionic acid (BPA) [60] are coupled to the free epoxy groups on the silicon-oxide-bound PGMA molecule. Instead, we couple 2-bromo-2-methylpropionyl bromide (BIBB) initiators to the hydroxyl group that is formed when PGMA epoxy-groups react with hydroxyl groups on the silicon surface. This leaves the non-reacted epoxy groups intact, which reduces the chance that water molecules reach the hydrolysis-sensitive surface bonds. Our prepared PGMA-PMPC brushes show excellent lubricating properties and degrafting-resistance in both water and aqueous salt media: The height of the PMPC brushes reduces by less than 1% after immersion in physiological (saline) and marine (0.6 M sodium chloride) environments for 4 weeks, while the brushes degraft by only 48% after immersion for 100,000 ppm hours in sodium hypochlorite solution. Our brushes, therefore, hold great potential for application in *e.g.* biomedical engineering or as low-fouling membrane-coatings.

2. Materials and methods

2.1. Materials

Azobisisobutyronitrile (AIBN, Aldrich, 98%) was recrystallized twice in methanol, and dried in the oven for 12 h at room temperature. Next it was kept in an amber flask, and stored in the fridge. Copper (I) bromide (CuBr, Aldrich, 98%) was purified by stirring in acetic acid and filtered till the suspension solution was pale like. After washing with ethanol, the powder was dried in a vacuum oven at room temperature overnight. Poly (glycidyl methacrylate) (PGMA, $M_n = 1 \times 10^4$), 2-Methacryloyloxyethyl phosphorylcholine (MPC, 97%), 2,2′-Bipyridyl (≥99%), triethylamine (TEA, ≥99%), 2-bromo-2-methylpropionyl bromide (BiBB, 98%), copper (II) bromide ($CuBr_2$, ≥99%), sodium fluoride (NaF, ≥99%), sodium chloride (NaCl, ≥99%), sodium iodide (NaI, ≥99.5%), sodium hypochlorite solution (NaOCl, 10%), $CDCl_3$ (99.8 atom% D) and D_2O (99.9 atom% D) were purchased from Sigma-Aldrich, and used as received without any purification. Methanol (absolute), sulfuric acid (95–97%), Methyl ethyl ketone (MEK) and dimethylformamide (DMF) were purchased from Biosolve. Hydrogen peroxide (H_2O_2) was purchased from Merck. MilliQ water was made from a MilliQ Advantage A 10 purification system (Millipore, Billerica, Ma, USA).

2.2. Methods

2.2.1. Synthesis of PGMA-PMPC

First, the silicon substrate surfaces were activated with Piranha solution. Then, the PGMA thin film was deposited on the cleaned substrates by dip coating in a concentration of 0.1% of PGMA in MEK solution, and dried in air. As reported before [59], increasing the aging time before annealing improved the thickness of PGMA film on the substrates. Here, all the samples were kept in petri-dish for the aging time of 48 h and then annealed for 30 min at 110 °C. The physically attached macromolecular film was removed by