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Surface modification of a silicate substrate by a “grafting from” methodology utilizing a perester initiator

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Abstract

The perester silane *t*-butyl peroxy-11-trichlorosilylundecanoate was synthesized by hydrosilylation of *t*-butyl peroxy-10-undecanoate with trichlorosilane. These radical initiators were covalently bound to the surface of silicate substrates by self-assembled monolayer (SAM) techniques. Several hydrophilic and hydrophobic acrylate monomers were successfully grafted onto the silicate substrate by in situ polymerization from the surface bound perester initiators. The polymer brushes were characterized by the ATR–IR, XPS, AFM and water contact angles. The results of the study indicate this “grafting from” technique can be used for the preparation of polymer layers with high graft density. While these surface-bound initiators function similarly to surface-bound azo initiators, the preparation of the surface-active perester is a simple, two-step synthesis.

Keywords: Nanolayer; Surfaces; Radical polymerization; Initiators; Polyacrylate; Atomic force microscopy

1. Introduction

Modification of silicate surfaces by the chemical attachment of a polymer has been proven to be an effective method for altering the interaction of solids with the external environments [1–3]. Surface modification has been used for tailoring the chromatographic properties of solid supports, to immobilize catalysts, create boundary lubricants, produce antifouling coatings and to enhance the biocompatibility of substrate surfaces [4–6]. In recent years, there have also been applications in drug-delivery, sensors, microfluidic devices, and capillaries [7–9]. Methods for surface modification include physisorption of block copolymers and grafting preformed end functionalized polymers to the substrate site (“grafting to”). However, in the “grafting to” technique, only a small amount of polymer can be immobilized to the substrate. A higher grafting density can be obtained by in situ formation of polymer chain from the surface (“grafting from”) [10]. Currently, most of the research on the “grafting from” technique has focused on the living polymerization methods, such as TEMPO-mediated radical, living anionic, atom transfer radical polymerization (ATRP); these methods start with a surface-immobilized initiator followed by monomer polymerization [11–14]. There are a few reports on

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surface grafting on a silicate substrate by conventional free-radical polymerization. Rühe and co-workers [15–17] have reported surface immobilization of an azo initiator onto a silicate substrate followed by polymerization of hydrophobic monomers, such as styrene or methyl methacrylate (MMA).

Typically for applications that involve glass capillaries or micro fluidic devices, surface modification involves polymerization of vinyl monomers that are often selected to the polarity of the surface. For example, the monomer γ–methacryloxypropyltrimethoxysilane (MAPs) is anchored to silicate substrate, and the vinyl group is copolymerized with vinyl monomer in the solution initiated by free radical initiators [9]. However, this method mostly produces free polymer and results in low grafting density. We speculate that surface immobilization of an initiator will produce much higher grafting density and be a more efficient method for surface modification. In this paper, we synthesized a perester silane precursor, immobilized the initiator on a silicate surface, and grafted a series of polymers. Free radical polymerization has been employed because of the well recognized advantages of monomer range and relatively simple experimental conditions.

Rühe and co-workers utilized azo initiator structures based on azoisobutyryl nitrile. They reported that the half-life of their surface-active AIBN-like initiator exhibited the same half-life as unmodified AIBN which corresponds to a 10 h half-life at 64 °C [17]. Here we report the use of perester initiators which have higher half-lives but in contrast only require a simple two-step synthesis.

2. Experimental

2.1. Materials

N,*N*′-Dimethyl acrylamide (DMA), methyl methacrylate (MMA), 2-hydroxyethyl acrylate (HEA), and 2-hydroxyl methacrylate (HEMA) were purified by passage through a column of activated basic alumina (Aldrich, 150 mesh). Acrylamide (AM), *t*-butyl hydroperoxide, potassium hydroxide (KOH), undecenoyl chloride, trichlorosilane, hydrogen hexachloroplatinate, ethanol, tetrahydrofuran (THF), sodium bicarbonate ($NaHCO_3$), and magnesium sulfate ($MgSO_4$) were obtained from Aldrich and used without further purification. All other reagents and materials were purchased from Fisher Scientific.

2.2. Synthesis of t-Butylperoxy-10-undecanoate

An aqueous solution of 70% *t*-butyl hydroperoxide (13 g, 0.1 mol) was placed into a 250 mL round flask equipped with a magnetic stirrer and sealed with a rubber septum. The flask was placed into an ice bath and 17 mL (0.12 mol) of a 30% KOH solution and 19 mL (0.09 mol) of undecenoyl chloride were slowly added, over 1 h, via a syringe pump. The mixture was allowed to warm to room temperature over 16 h. The organic layer was separated and washed with 5% of $NaHCO_3$, twice with 30 mL water and dried over anhydrous $MgSO_4$. Evaporation and chromatography on silica gel with 10:1 hexane/ethyl acetate (v/v) yielded 14.5 g of a clear oil. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 5.8 (m, 1H, $=CH$), 5.0 (m, 2H, $CH_2=$), 2.3 (t, 2H, CH_2-CO), 2.0 (q, 2H, CH_2-CH=), 1.7 (m, 2H, CH_2-CH_2-CO-), 1.2–1.5 (m, 19H, (-CH_2)$_5$-, O-C-(CH_3)$_3$).

2.3. Preparation of t-Butyl peroxy-11-trichlorosilyundecanoate

A solution of 1 g (4 mmol) *t*-butylperoxy-10-undecanoate in 20 mL THF was placed in a 50 mL round bottom flask equipped with a magnetic stir bar, sealed with a rubber septum and purged with argon. A solution of 20 mg of hydrogen hexachloroplatinate in 0.05 mL of ethanol was added. The solution was cooled in an ice bath and 0.6 mL (6 mmol) of trichlorosilane was added. The solution was allowed to warm to room temperature over 5 h. Volatiles were removed under vacuum, producing 0.95 g yellow oil. The residual catalyst was removed by stirring a CH_2Cl_2 solution of the product over anhydrous Na_2SO_4 for 20 min followed by filtration. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 2.3 (m, 2H, CH_2-CO), 1.7 (m, 2H, CH_2-CH_2-CO), 1.2–1.5 (m, 23H, (CH_2)$_7$, O-C-(CH_3)$_3$), 0.6 (t, 2H, Si-CH_2).

2.4. Monolayer deposition

Silicate substrates were placed into the solution of concentrated sulfuric acid and 30% of hydrogen peroxide (70:30 v/v) and heated at 60–90 °C for 1 h. Substrates were then removed from the solution and rinsed with a large amount of distilled water followed by ethanol and dried with air. Silicon wafers were then immediately immersed into an appropriate deposition solution. A typical deposition solution was prepared by mixing 0.2 mL silane with 20 mL of toluene for 10 h at room temperature.