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Robust grafting of PEG-methacrylate brushes from polymeric coatings

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ABSTRACT

A study is presented of the grafting of poly(ethylene glycol)methyl ether methacrylate (PEGMA) from polymeric macroinitiator films to form well-defined polymer brushes, using activators generated/regenerated by electron transfer (AGET/ARGET) atom transfer radical polymerization (ATRP). Polymer brush coatings can potentially be obtained on surfaces of virtually any shape and composition, because of the ease of conformal casting of the anchoring macroinitiator film. Polymer brush coatings are synthesized in a robust way, as ARGET and AGET ATRP require little to no deoxygenation and make use of stable catalysts. The monomer, catalyst, ligand and reducing agent concentrations, the amount and type of initiating moiety in the anchoring films, and the choice of solvents are optimized, resulting in control over the rate of reaction, and the molecular weight of poly(PEGMA). The best conditions are determined for the formation of a poly(PEGMA) brush with high grafting density, controlled thickness and “living” ends available for post-functionalization.

1. Introduction

Polymer brush coatings are composed of end-tethered chains closely packed together. This configuration confers unique properties to surfaces, such as low fouling, low friction, resistance to corrosion and controlled wettability [1]. The most commonly used strategy to tether polymer chains to a surface, with a grafting density high enough to produce a brush conformation, is the “grafting-from” technique [2–4]. In this method, a low molecular weight initiator moiety is generally covalently bound onto the surface, from which polymer chains grow. This involves non-trivial chemical modifications of the surface, which are suitable only for surfaces with a specific chemistry (e.g. silane coupling onto silicon oxide, thiol coupling onto gold). A more versatile strategy involves the use of polymeric macromolecules that incorporate the initiators required for the surface-initiated polymerization. Thin films of macroinitiators can be readily applied to a variety of surfaces, with different chemistries and geometries, using techniques such as spin-coating or dip-coating from solution. This strategy makes the immobilization of initiator moieties to a surface quick, simple and easily adaptable to large surface areas, complex geometries and different chemical compositions. The use of polymer films as anchoring layers for the grafting of polymer brushes has recently attracted great interest. Many of the examples in the literature involve the use of insoluble, cross-linked macroinitiator films [5–11], and only little work has been published on the use of linear macroinitiator films, prepared either by layer-by-layer deposition [12] or by spin-coating [13,14]. Uncross-linked macroinitiator films are easier to prepare, as they do not require the incorporation of additional functional groups for cross-linking, and have the advantage of retaining their ability to rearrange themselves under certain stimuli (e.g. heat). We have recently demonstrated that this ability could be exploited to spontaneously pattern a macroinitiator film by dewetting upon annealing, and hence transfer the pattern to the polymer brush coating grown from it [15]. Dewetting is a spontaneous process that can produce patterns of holes with controlled size and density [16,17].

Grafting from uncross-linked polymeric macroinitiator films requires some sensible design, as the polymerization conditions to grow the desired brush have to be tailored in order to avoid film damage. The versatility of using a polymer film comes at the cost of having a more fragile initiator coating, which is not covalently bound to the surface but relies on physico-chemical forces for adhesion to the substrate material. We report here a study of the grafting of poly(ethylene glycol) methyl ether methacrylate (PEGMA) from different macroinitiator films incorporating initiators that are suitable for ATRP. PEG-like polymers such as these are often used in biomedical

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applications for their biocompatibility and low fouling properties [18–22]. Radical polymerization of vinyl monomers containing PEG is much easier to control compared to anionic polymerization (required to grow PEG chains with controlled molecular weight), both in solution [23] and initiated from a surface [24]. The use of ATRP allows for the formation of brushes with controlled thickness and which bear post-functionalizable ends for further tailoring of the coating [3].

PEGMA monomers have been extensively used to prepare low-fouling polymer brushes by ATRP. For a comprehensive review of ATRP of PEGMA see the work from Lutz [25]. PEGMA has been grafted from a wide variety of materials, such as poly(tetrafluoroethylene) membranes [26], poly(ethylene terephthalate) films [27], polyethylene films [28], and poly(dimethylsiloxane) sheets [29]. In recent studies, PEGMA's thermo-responsiveness was exploited for controlled drug transport through a membrane [30], and for switchable cell attachment [31]. It is important to stress that all these approaches required chemical modification of the surfaces with ATRP initiators.

In this work, two robust variations of ATRP were employed, namely activators regenerated by electron transfer (ARGET) [32] and activators generated by electron transfer (AGET) ATRP [33]. Both these techniques are less sensitive to oxygen than other controlled radical polymerizations, as only the stable copper (II) catalyst is employed, while the unstable copper (I) is formed *in situ* by means of a reducing agent. This simplifies the reaction procedure, as it allows polymerization to occur in the presence of limited amounts of air, eliminating the need for careful deoxygenation of the reaction medium [34]. In the case of ARGET ATRP, the fast electron transfer between the copper and the reducing agent limits the side reactions that can poison the catalyst. Thus only very small amounts of catalyst are required, facilitating purification of the product.

In this paper, we focused on: 1) engineering the mildest conditions for the polymerization of PEGMA, in order to avoid damage to the macroinitiator film; 2) achieving control of the surface-initiated ATRP of PEGMA under such mild conditions, by investigating the effect of catalyst, ligand and reducing agent concentrations on the resulting molecular weight and dispersity of poly(PEGMA) in both ARGET and AGET ATRP.

2. Experimental

2.1. Synthesis of the M1 macroinitiator

A dry 4 mL glass tube was charged with 2-(2-chloropropanoyloxy)ethyl methacrylate (MMA-Cl; 280 mg, 1.2 mmol), methyl methacrylate (MMA; 720 mg, 7.2 mmol, Sigma–Aldrich), toluene (0.17 mL) (>99.9%, Sigma–Aldrich), doubly recrystallized azobis(isobutyronitrile) (AIBN; 1.39 mg, 8.46 μmol) and 2-cyanopropan-2-yl dithiobenzoate (CPDB; 8.95 mg, 40.4 μmol). The tube was sealed with a rubber septum, and the mixture was deoxygenated by bubbling nitrogen for 5 min at 0 °C. The glass tube was then immersed in an oil bath at 70 °C and left to react with stirring for 17 h. The reaction was stopped by cooling the vial to room temperature and exposing the contents to air. The viscous product was diluted in toluene and precipitated in cold methanol. The polymer powder was dried under vacuum at room temperature. Size exclusion chromatography (SEC) calibrated with poly(methyl methacrylate) standards in tetrahydrofuran (THF) was used to determine the molecular weight of the product: M_n = 23,800 g mol^{-1}, Đ = 1.27. The composition of the polymer was determined by ^{1}H NMR: 19.6% MMA-Cl and 80.4% MMA (Figure S1 in the Supporting Information – SI). See Fig. 1 for reaction scheme.

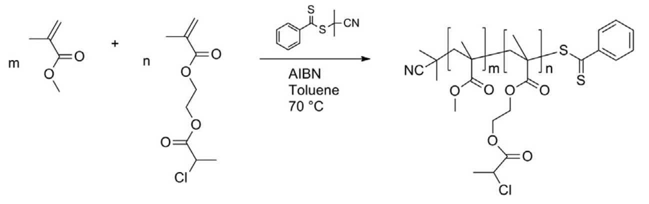

Fig. 1. Reaction scheme of the RAFT reaction used to produce the macroinitiator M1.

2.2. Synthesis of the M2 macroinitiator

A dry 4 mL glass tube was charged with 2-(2-bromopropanoyloxy)ethyl methacrylate (0.7 mL, 3.77 mmol), toluene (0.7 mL) (>99.9%, Sigma–Aldrich), doubly recrystallized AIBN (0.6 mg, 3.6 μmol) and CPDB (8.0 mg, 36.3 μmol). The tube was sealed with a rubber septum, and the mixture was deoxygenated by bubbling nitrogen for 5 min at 0 °C. The glass tube was then immersed in an oil bath at 65 °C and left to react with stirring for 22 h. The reaction was quenched by cooling the vial to room temperature and exposing the contents to air. The product was purified and characterized as above. The molecular weight of the product was: M_n = 20,700 g mol^{-1}, Đ = 1.28. See Fig. 2 for reaction scheme.

2.3. Film preparation

The substrates used to support the polymer films were silicon wafers with a native oxide layer (MMRC Pty Ltd, Malvern VIC Australia), typically 1.5 × 1.5 cm^2. The substrates were cleaned as per procedure reported elsewhere [35].

Polymer films were cast on the silicon substrates by spin-coating (Laurell Technologies Co., PA). Immersion in typical reaction media of M1 and M2 macroinitiator films cast directly onto silicon resulted in delamination, therefore an interlayer of polystyrene was used to increase the adhesion of the poly(methacrylate) macroinitiator films onto the substrate. Polystyrene (M_n = 96,000 g mol^{-1}, Đ = 1.04; Polymer Standards, Germany) was spin-cast in films on the clean silicon wafers from a 15 mg mL^{-1} filtered toluene solution (3000 rpm for 1 min). Macroinitiator films were then spin-cast on top of the PS films from a 10 mg mL^{-1} acetonitrile (>99.9%, Merck) solution (4000 rpm for 1 min), acetonitrile being a non-solvent for PS. The average thickness of the films obtained was 58 ± 1 nm for PS and 28 ± 1 for the macroinitiators, as determined by spectroscopic ellipsometry (J. A. Woollam Co.). The refractive index of each individual layer was fitted together with its thickness. The resulting refractive index was compared to literature values to confirm both the quality of the fitting and the identity of the polymer film. All poly(PEGMA) layers characterized had refractive index of 1.45 ± 0.01, which was consistent with the reference value for PEG of ~1.46 (manufacturer website). The topography of the films and of the grafted brushes was investigated by Tapping Mode atomic force microscopy in air

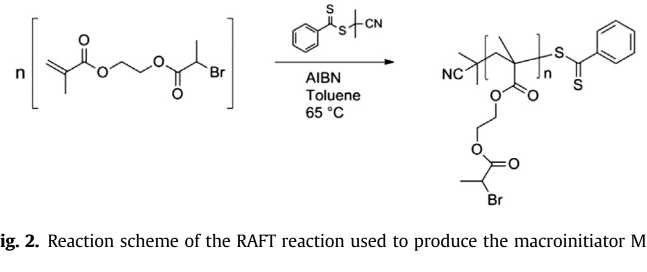

Fig. 2. Reaction scheme of the RAFT reaction used to produce the macroinitiator M2.