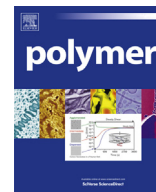




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Clickable poly(ionic liquid)s for modification of glass and silicon surfaces

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ABSTRACT

Covalent attachment of poly(ionic liquid)s (PILs) by click chemistry on glass or silicon (Si) surfaces was performed. Poly[1-(4-vinylbenzyl)-3-butylimidazolium bis(trifluoromethylsulfonyl)imide] (poly-VBBI⁺Tf₂N⁻), and copolymers of polyVBBI⁺Tf₂N⁻ with fluorescein *O*-methacrylate were synthesized by conducting an atom transfer radical polymerization (ATRP) from initiators containing azide or thioacetate groups. The azide- and thiol-terminated PILs were then successfully grafted onto alkyne and alkene modified glass/Si wafers by thermal azide–alkyne cycloaddition and photoinitiated thiol–ene click reactions, respectively. The modified surfaces were characterized by contact angle measurements and ellipsometry. The fluorescent PIL functionalized surfaces showed strong fluorescence under UV irradiation. This procedure of tethering PILs to substrates also provides an easy way to change the surface hydrophilicity by replacing the anions in the grafted PILs. The present approach could be readily applied for surface modifications with other types of PILs or their copolymers to achieve different functionalities on various surfaces.

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1. Introduction

Poly(ionic liquids) (PILs) are different from uncharged polymers in a number of important respects. PILs combine the highly desirable properties of ionic liquids (tunable solubility, negligible vapor pressure, wide electrochemical window, and high thermal stability) with ease of incorporating functionality and processability of polymers [1–4]. This combination of properties has led to the use of PILs in membranes, electrochemical devices, micelles, and gels [5–9].

If appropriate synthesis and modification techniques are utilized, PILs have the potential to be used successfully in a variety of surface modification applications. Properties that could be modified include friction, hydrophobicity, adhesion, corrosion, etc. Indeed, these materials have already found use in applications such as water repellents [10], anti-bacterial, and anti-biofouling materials [11].

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Glass and silicon (Si) are commonly used substrates for surface modification. It is easy to introduce various small functional groups onto their surfaces by organosilane reactions. The surface functional groups can serve as initiating sites that can either initiate polymerizations via the “grafting from” approach, or act as the anchoring sites that can react with other species via the “grafting onto” approach [12–16]. The controlled/living radical polymerization (CRP) techniques, especially surface-initiated atom transfer radical polymerization (SI-ATRP) [17–21], are powerful methods to grow polymers from surfaces. SI-ATRP has been developed over the last decade to build functional macromolecules on glass/Si surfaces, resulting in temperature-responsive polymer modified surfaces [22,23], non-fouling and biocompatible surfaces [19,24–27]. In addition, functional polymers have been covalently grafted onto glass/Si surfaces to construct pH-responsive surfaces through the reactions between the hydroxyl groups in the polymers with the surface acyl chloride groups [28], and non-leaching antibacterial surfaces through the reactions between the trimethoxysilyl groups in the polymers and the surface silanol groups [29]. Also, click chemistry was widely used in the “grafting onto” approach for the grafting of a variety of polymer brushes to solid substrates [30–38].

Herein, we demonstrated the applicability of PILs for modification of glass and silicon surfaces. A styrenic imidazolium ionic

liquid monomer was polymerized by ATRP [39] using functional initiators to produce clickable PILs containing azide or thiol terminal groups. In addition, to evaluate the quality of the surface modification PIL copolymers were prepared by copolymerization of fluorescein *O*-methacrylate and the ionic monomers. The clickable PILs were grafted onto glass and silicon surfaces that had been modified with alkyne or alkene groups using organosilane reactions. While the “grafting onto” technique allows for well-defined polymers with different architectures and components to be synthesized first and consequently immobilized on the surfaces, it usually results in lower grafting density and less uniform grafting compared to the “grafting from” technique [29]. However, the mild conditions of click reactions avoid the need to employ strict “grafting from” polymerization conditions for the surface functionalization. Click chemistry is characterized by its modular nature, rapid reaction rates, high yield and conversion, and high selectivity, which make it a facile and versatile strategy for (macro-) molecular synthesis and surface functionalization [40–55]. Both thermal azide–alkyne cycloaddition [56,57] and photoinitiated thiol–ene radical reaction [58–61] were successfully used for the efficient immobilization of PILs onto the modified surfaces. The fluorescent PIL copolymers modified surfaces showed strong fluorescence under UV irradiation. Water contact angle measurements showed that the hydrophilic/hydrophobic properties of the glass/Si surfaces were changed by grafting with PILs, poly(ethylene glycol) (PEO), or by ionic exchange from Tf_2N^- to Cl^- . This surface modification approach based on clickable PILs is facile, efficient, and easily applicable to other types of surfaces modified with different PILs for many specific applications.

2. Experimental

2.1. Materials

1-Butylimidazole (98%), bis(trifluoromethylsulfonyl)imide lithium salt (LiTf_2N , $\geq 99\%$), butyronitrile (99%), ethyl 2-bromoisobutyrate (EBIB, 98%), N,N,N',N',N' -pentamethyldiethylenetriamine (PMDETA, 99%), fluorescein *O*-methacrylate (97%), 2-bromoisobutyryl bromide (98%), 3-chloro-1-propanol (98%), thioacetic acid (96%), triethylamine ($\geq 99.5\%$), 1,5-hexadiene (97%), (3-aminopropyl)trimethoxysilane (97%), 5-hexynoic acid (97%), *N*-hydroxysuccinimide (NHS, 98%), 4-dimethylaminopyridine (99%), 2,2-dimethoxy-2-phenyl acetophenone (DMPA, 99%), poly(ethylene glycol) ($M_n \sim 4600$ and 400), lithium chloride (99%), *p*-toluenesulfonic acid monohydrate (98%), 3-mercaptopropionic acid ($\geq 99\%$), and Karstedt's catalyst solution (Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene, Pt $\sim 2\%$, 0.1 mL) were purchased from Aldrich. Pyrrolidine ($\geq 99\%$) was purchased from Acros Organics. Triethoxysilane (96%) and 3-chloro-1-propanol (98%) were purchased from Alfa Aesar. *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC•HCl, $\geq 98\%$) was purchased from Carbosynth. 4-Vinylbenzyl chloride (90%) were purchased from Aldrich and purified by passing over a column of basic alumina to remove the inhibitor. CuBr and CuBr_2 were purchased from Aldrich in the highest available purity. All solvents and chemicals are of reagent quality and were used as received unless special explanation. Pre-cleaned glass slides were purchased from Corning. A heavily doped n-type Si substrate, with a thermally grown 250 nm silicon dioxide layer, was purchased from MEMC Electronic Materials, Inc. 3-Azidopropyl 2-bromoisobutyrate and 3-azidopropyl 2-bromo-2-methylpropanoate ($\text{N}_3\text{-Br}$) was synthesized according to previously published procedures [16,55]. Thiolated PEG (PEO–SH, $M_n \sim 4600$ g/mol) was synthesized according to previously published procedures [62]. Azido-terminated PEO (PEO– N_3 , $M_n \sim 400$ g/mol) was synthesized

according to previously published procedures [48]. The ionic monomer, 1-(4-vinylbenzyl)-3-butyylimidazolium bis(trifluoromethylsulfonyl)imide] ($\text{VBBI}^+\text{Tf}_2\text{N}^-$), was synthesized according to previously published procedures [63].

2.2. Synthetic procedures

2.2.1. Synthesis of 3-(acetylthio)propyl 2-bromo-2-methylpropanoate (AcS-Br)

3-Chloro-1-propanol (15.00 g, 159 mmol), anhydrous diethyl ether (50 mL), and triethylamine (16.86 g, 167 mmol) were added to a three-neck round-bottom flask equipped with a dropping funnel. After the flask was immersed to an ice-water bath, a solution of thioacetic acid (12.68 g, 167 mmol) in anhydrous CH_2Cl_2 (20 mL) was added dropwise to the solution. The reaction was stirred at 0 °C for 1 h and then at r.t. for 24 h. The reaction mixture was then filtered, and washed with deionized water. The organic phase was dried over anhydrous Mg_2SO_4 overnight, and then the CH_2Cl_2 was removed by rotary evaporation. The product was further purified by silica gel column chromatography (ethyl acetate/hexane: 1/9 (v/v)). $^1\text{H NMR}$ (300 MHz, CDCl_3): δ (ppm) = 1.84 (2H, m), 2.37 (3H, s), 3.02 (2H, t), 3.67 (2H, t).

3-Hydroxypropyl thioacetate (4.00 g, 29.8 mmol), anhydrous CH_2Cl_2 (40 mL), and triethylamine (3.62 g, 35.8 mmol) were placed in a three-neck round-bottom flask equipped with a dropping funnel. After the flask was immersed in an ice-water bath, a solution of 2-bromoisobutyryl bromide (8.22 g, 35.8 mmol) in anhydrous CH_2Cl_2 (10 mL) was added dropwise to the flask. The reaction was stirred at 0 °C for 1 h and then at r.t. for 24 h. The reaction mixture was filtered, then washed successively with NaHCO_3 and deionized water. The organic phase was dried over anhydrous Mg_2SO_4 overnight, and then the CH_2Cl_2 was removed by rotary evaporation. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ (ppm) = 1.95 (6H, s), 2.01 (2H, m), 2.35 (3H, s), 2.98 (2H, t), 4.24 (2H, t).

2.2.2. Synthesis of clickable PILs

Typically, the ionic monomer (or a mixture of ionic liquid monomer and fluorescein *O*-methacrylate), initiator ($\text{N}_3\text{-Br}$ or AcS-Br), CuBr_2 , PMDETA, and butyronitrile were added to a Schlenk flask. The flask was then degassed by five freeze–pump–thaw cycles. During the final cycle, while the contents were frozen in liquid nitrogen, the flask was back filled with nitrogen and CuBr was added. The flask was then degassed and back filled with nitrogen thrice. The flask was allowed to warm up to room temperature and an initial sample was collected by syringe. The flask was then placed in an oil bath thermostated at 90 °C. Samples were taken from the flask at timed intervals for GPC and NMR measurements. The polymerization was stopped by opening the flask and exposing the catalyst complex in the solution to air. The polymer was precipitated by addition of the reaction solution to methanol/water (4/1, v/v), purified by dialysis against THF, and dried in vacuum at room temperature overnight. 1.0 g of the as-prepared PILs, synthesized using AcS-Br as initiator, was mixed with pyrrolidine (0.14 g) in THF (10 mL) under nitrogen. The mixture was stirred at room temperature under nitrogen for 1 d. The polymer was purified by dialysis against THF, and dried in vacuum at room temperature overnight.

2.2.3. Modification of glass and silicon surfaces with alkyne and alkene groups

The glass slides and silicon wafers were treated with piranha solution ($\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2$, 4:1) for 2 h. (Warning: Piranha solution reacts violently with organic materials and it should be freshly prepared before use and disposed of properly. Do not store or combine

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