Surface Functionalization with Polymer and Block Copolymer Films Using Organometallic Initiators

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Surface-initiated graft polymerization has been shown to be an efficient method for functionalizing solid surfaces for controlled adhesion, lubricity, biocompatibility, and many other purposes.[1] Radical, cationic, anionic, and organometallic-based initiation have all been demonstrated to be successful routes to such surface-grafted polymer films.[1b−h] Surface-bound organometallic ROMP catalysts have been shown to be able to initiate in a "living" manner the polymerization of cyclic olefins with the catalytic site at the end of the growing polymer chain, allowing for possible surface functionalization by selective chain termination, or for possible block copolymerization.[1d] This work describes a novel system for initiation of surface-grafted polymerization: the use of lanthanide organometallic catalysts to surface-graft polymer brushes of common, commercially important, noncyclic olefins. These organometallic surface polymerization initiators can also provide the advantages of "living polymerization", block copolymerization of both nonpolar and functionalized monomers, and chemical tailoring of the polymer films' surfaces, for optimized functionality.

We have shown previously that homogeneous, robust and uniform silane monolayers can be generated on a variety of oxide surfaces.[2] A layer of 5-hexenylsilane (or any of several vinyl-terminated silane layers) was generated on a silicon surface by reaction of a 5-hexenyltrichlorosilane precursor with the pretreated surface, as previously described.[2] These functionalized silicon substrates were exposed to a THF solution of $(C_{10}H_{15})_2Sm(THF)_2$[3] over a period of 1 to 3 days. It has been shown that, in solution, this complex reduces vinyl groups to form Sm-bound allyls,[4] which are efficient polymerization catalysts for a variety of olefins.[5] The substrates were then removed from the THF solution, rinsed, and placed in an atmosphere of 1200 psi of ethylene. After 12 to 72 h, the substrates were removed from the reaction apparatus, rinsed with methanol, and dried in air.

Examination of the silicon surfaces by ATR FTIR spectroscopy and profilometry showed that films of polyethylene had formed on the silicon surfaces, of approximately 90 nm thickness (Figure 1). The films varied in smoothness, showing average rms roughness of 565 Å over a 2×10^6 Å scan range. IR bands at 1098, 1060, and 1016 cm^{-1} (see inset, Figure 1) demonstrate
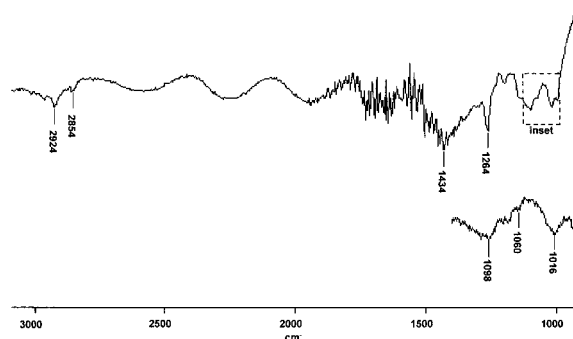
Figure 1. ATR FT-IR (Ge crystal) spectrum of polyethylene surface-grafted from a silicon substrate using the samarocene initiator shown in Scheme 1.

covalent bonding of the polymer to the silicon surface via Si−O−Si linkages, as well as siloxane network modes.[6] These films could not be removed by application of a pressure-sensitive adhesive, showing strong adhesion to the silicon surface. When a control experiment was performed using a nonfunctionalized silicon substrate, the polyethylene that adsorbed on the silicon surface was completely removed by application of adhesive tape. Better adhesion of polyethylene films to a variety of inorganic substrates has been a topic of intense research; this surface-initiated grafting of polyethylene to form robust, strongly attached films may provide much enhanced control over the polymer/substrate interface.[7]

In another experiment, a toluene solution of the known ethylene polymerization catalyst precursor $Tp^{Me}YCl_2(THF)$[8] was exposed for 7 days at −30° C to a silicon surface that had been functionalized with a propyllithium monolayer.[2] The substrate was again rinsed, dried, and exposed to 900 psi of ethylene. After 24 h the reaction was terminated as described above, and the silicon surface was again found to be functionalized with a strongly bound surface-grafted film of polyethylene. These films proved to be much more rough and patchy than those produced by the Sm initiator, probably due to the steric bulk of the active polymerization catalyst formed at the silicon surface (see below).

Due to the wide range of functionalized monomers polymerized by Sm alkyl and allyl complexes,[5] we exposed the Sm-treated 5-hexenyl silicon surfaces to neat methyl methacrylate for periods ranging from 1 to 9 days. After rinsing and drying of the substrates, the surfaces were found to be functionalized with films of poly(methyl methacrylate) of thicknesses ranging from 30 to 130 nm (by profilometry), with film thicknesses increasing with increased reaction time. The identity of the surface-grafted polymer films was established by XPS and reflectance FTIR spectroscopy (Figure 2), which are both consistent with PMMA reference spectra.[9] The Si$_{surface}$−O−Si stretch at 1060 cm^{-1}, which was observed in the surface-grafted polyethylene spectra, is obscured in these IR spectra by the 1064 cm^{-1} band of PMMA. The films are also robust and cannot be removed from the silicon by application of a pressure-sensitive adhesive, again demonstrating strong attachment of the polymer brushes to the silicon surfaces.

The active polymerization site that is hypothesized for these surface functionalizations is the formation of a surface-bound Sm allyl (Scheme 1) or a surface-bound Y alkyl (Scheme 2).

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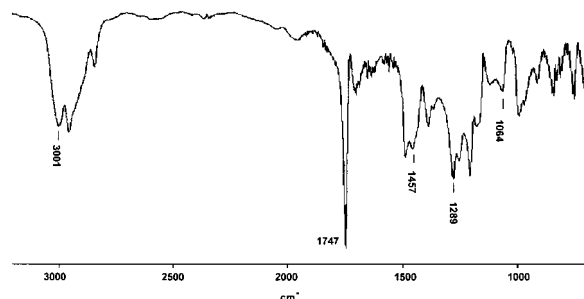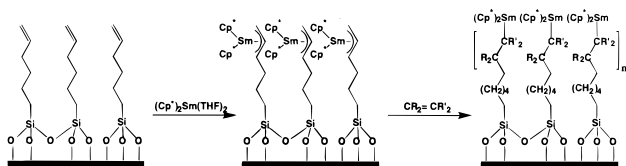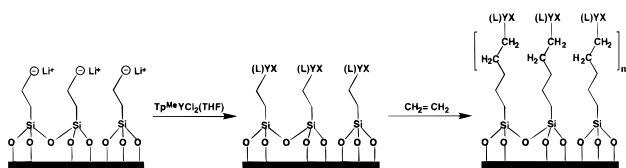
Figure 2. Grazing angle FT-IR (80°) spectrum of poly(methyl methacrylate) surface-grafted from a silicon substrate using the samarocene initiator shown in Scheme 1.

Scheme 1. Proposed Generation of the Active Sm Catalyst on the Substrate Surface

Scheme 2. Proposed Generation of the Active Y Catalyst on the Substrate Surface

Because of the extreme steric demands of the large Tp^{Me} ligand and the Y complex's crowded coordination sphere, this polymerization initiator should be less active when attached to a surface, as was observed. Insertion polymerization, analogous to that initiated by such complexes in solution, then occurs, allowing the formation of the strongly surface-bound polymer brushes. Examination of the IR spectra of the grafted PMMA homopolymer (and the PMMA block of the grafted copolymer described below) shows some degree of syndiotacticity,[10] as was seen in the PMMA produced by this catalyst in solution.[5c] Because polymerization by lathananide initiators in solution has been found to approach ideal "living" conditions (lack of chain transfer and termination mechanisms), these organometallic polymerization initiators should be able to produce polymer brushes that are thicker and more homogeneous (less chain branching) than the polymer brushes generated by conventional free-radical surface initiation. These organometallic polymerization initiators are able to efficiently polymerize monomers as different as nonpolar ethylene and an ester-functionalized olefin,[5a] so a much wider range of polymer-functionalized surfaces should be attainable than can be achieved using anionic surface initiators. Unlike supported heterogeneous olefin polymerization catalysts,[11] organometallic surface intiation polymerization leaves the active catalytic site on the distal end of the growing polymer chain, and so the everthickening layer of already-formed polymer will not impede insertion of fresh monomer.[1d] Cleavage of the polymer chain from the metal center in the termination step of the polymerization could be done with a wide variety of reagents, thus producing

surface-bound polymer films that present a designed reactive site at the outer surface. This could be used to design interfaces of specific functionality for a variety of applications, especially in fabrication of biomaterials.

This surface-initiation polymerization method can also produce surfaces functionalized with block copolymer films. Copolymers composed of functional and nonpolar blocks have been an important goal in olefin polymerization chemistry, with few initiators reported that can tolerate and efficiently polymerize such monomers.[5a,12] Such block copolymers grafted onto ceramic or polymer surfaces would be of great use in tailoring hydrophobic/hydrophilic properties to optimize the adhesion, dyeing, moisture-absorbing, biocompatiblity, and other properties of ceramic surfaces. A hydrophobic/hydrophilic block copolymer has recently been shown to have remarkable properties as an artificial vesicle, and might be useful as an artificial membrane when grafted onto a surface.[13] We therefore attempted to produce surfaces functionalized with grafted block copolymer films using the organometallic surface initiators described above. Polyethylene films were generated on silicon substrates using the Sm-based initiator described above. The substrates were partially immersed in neat, freshly distilled, methyl methacrylate, such that half the substrate was suspended in the neat monomer, while the other half remained above the liquid. After 6 days, visible differences between the films covering the two halves of the substrates were observed. The substrates were then rinsed, dried, and examined by IR spectroscopy and profilometry. The portions of the substrates exposed to MMA were found to have films of PMMA on the surfaces, which were approximately 1.0 μm thick (total polymer film thicknesses were approximately 1.1 μm on the portions of the substrates exposed to both ethylene and MMA), while the portions unexposed to MMA showed only polyethylene.

This organometallic initiation system can therefore produce surfaces functionalized with robust, strongly bound, grafted polymer films composed of an underlying polyethylene block and a surface PMMA block. With such a surface that is catalytically active toward common, noncyclic, polar, and nonpolar monomers, a wide variety of specifically engineered surfaces may be obtained, including the production of hydrophilic/hydrophobic block copolymer films. Work is ongoing to tailor reaction conditions for production of optimized silane monolayers, surface-bound organometallic initiators, and polymer film thickness and properties. Also, the use of a variety of surface-bound organometallic initiators, and polymerization and block copolymerization of a variety of monomers is being studied in order to produce a variety of ceramic and polymer surfaces of specifically designed functionality.

Supporting Information Available: Experimental details, time versus thickness studies of grafted PMMA, IR spectra of the grafted PE/PMMA copolymer (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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