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New Syntheses of Hyperbranched Polyamine Grafts

David E. Bergbreiter,* Andrew M. Kippenberger, and William M. Lackowski

Texas A&M University, Department of Chemistry, P.O. Box 30012, College Station, Texas 77842-3012

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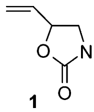
ABSTRACT: This paper describes a new synthesis of hyperbranched polyamine grafts on amine functionalized silicon wafers using a surface-initiated palladium-catalyzed ring-opening graft polymerization of 5-vinyl-2-oxazolidinone. The extent of grafting was followed by contact angle analysis, ATR−IR, and XPS spectroscopy. The surface mechanical properties of the resulting interfaces were characterized physically using a nanoindenter. The surface roughness of the grafts was measured using atomic force microscopy. Analogous solution-state palladium-catalyzed polymerizations of 5-vinyl-2-oxazolidinone were also investigated using isobutylamine as an initiator to provide insight into the structure of the graft polymer.

Introduction

Our group has pursued the synthesis of functional surfaces through hyperbranched grafting primarily using poly(*tert*-butyl acrylate) to prepare hyperbranched poly(acrylic acid) grafts. This chemistry works well with a variety of substrates.[1−5] Extensions of this chemistry that use reductions and repetitive Ce(IV)-based radical grafting reactions of acrylic acid as a monomer work about as well as a route to similar hyperbranched carboxylic acid containing hyperbranched grafts.[6,7] The carboxylic acid-rich interfaces produced by either of these methods are useful intermediates in that they can be derivatized to form other grafts or a variety of other functional groups.[5] Supported thin films of acidic (or basic) groups are generally useful as precursor substrates in layer-by-layer chemistry.[8] Our group and others have shown that such carboxylic acid containing surfaces also have utility in catalyst synthesis after ion exchange and reduction of entrained transition metal salts.[9,10] However, while there are successful routes to ultrathin covalent assemblies of carboxylic acid groups, alternative syntheses of hyperbranched grafts remain of interest. We are also particularly interested in syntheses that lead directly to basic aminated surfaces as amine-containing surfaces have reactivity that is complementary to the carboxylic acid containing surfaces available from this existing chemistry. This paper describes one such synthesis—a hyperbranched ring-opening polymerization.

The chemistry described here has a parallel in a previously reported synthesis of hyperbranched poly(ethylenimine) on silicon using ring-opening of aziridine by interface-bound nitrogen nucleophiles.[11,12] This new grafting chemistry differs from that earlier work in that the chemistry described here depends on transition metal catalysis of ring opening of a nonnucleophilic monomer. Transition metal-catalyzed surface grafting that depends on a surface-confined growing chain has also been used previously. For example, ruthenium complexes are used in metathesis-based grafting,[13] and copper complexes are widely used in ATRP-grafting (atom-transfer radical polymerization).[14,15] The chemistry described here uses Pd(0) catalysts and Pd-catalyzed allylic substitution reactions that are widely used in organic synthesis,[16] applying these reactions to allylic substitution of a nitrogen-containing monomer derived from the readily available commodity chemical 1,2-epoxybutadiene.[17] Specifically, this paper describes the surface-initiated palladium-catalyzed ring-opening polymerization of 5-vinyl-2-oxazolidinone (VOX, **1**). The hyperbranched poly(1-aminobutadiene) (PVOX) grafts prepared from this monomer require an amine-containing surface as a precursor; this work used amine-functionalized silicon wafers as initiators for this surface grafting. Complementary solution-state polymerizations of 5-vinyl-2-oxazolidinone were carried out using isobutylamine as an initiator and the products were studied by ^{1}H NMR spectroscopy to provide insight into the structure of the polymer grafts.



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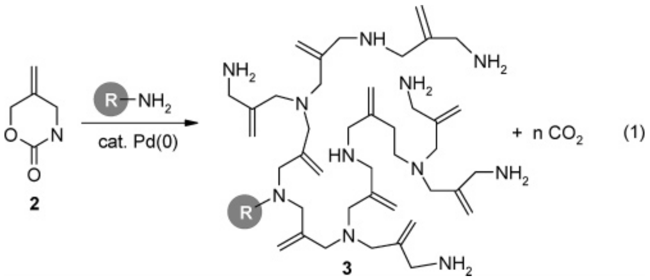
The concept of using an unsaturated cyclic carbamate monomer to produce hyperbranched polyamines was first described by Suzuki's group.[18,19] This group described the polymerization of monomer **2** using palladium-catalyzed ring-opening polymerization (eq 1).



(1)

The polymerization is believed to occur by initial oxidative addition of Pd(0) to the vinyl carbamate **2.** Subsequent nucleophilic attack by a nucleophilic initiator (i.e., the amine initiator) on the π-allylpalladium complex so formed then leads to a new N−C bond and a carbamic acid derivative of an allylic amine. Loss of CO_2 from this carbamic acid derivative leaves behind a primary amine. Either these primary amines or the secondary amines formed in the original nucleophilic attack on the π-allylpalladium complex then can react further in chain propagation steps, attacking other π-allylpalladium complexes. This results in a hyperbranched polymer with the initiator as the core (or base in the case of a surface-bound initiator).

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* Corresponding author. Bergbreiter@tamu.edu.

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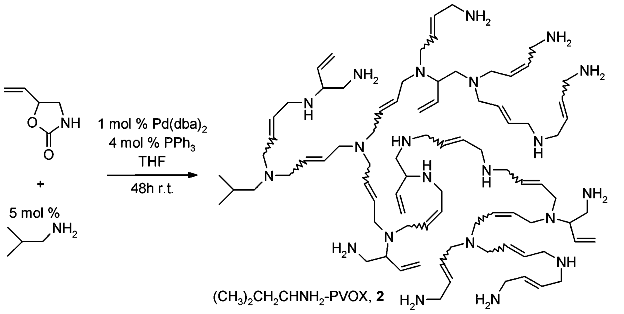
The catalytic chemistry described below extends this earlier work and leads directly to a hyperbranched polymer through a cascade of reactions that double the number of sites for reaction at each stage using nitrogen's trivalent character as a basis for the hyperbranching. The results described in this work show that this Pd-catalyzed allylic substitution chemistry is as useful at surfaces as it is in solution. While monomer **2** can be prepared in several steps from commercially available 3-chloro-2-chloromethyl-1-propene,[20] we were able to obtain the analogous oxazolidinone monomer **1** from Eastman Chemical. Thus, we have examined the utility of this monomer in surface graft chemistry. The results of this study are described below.

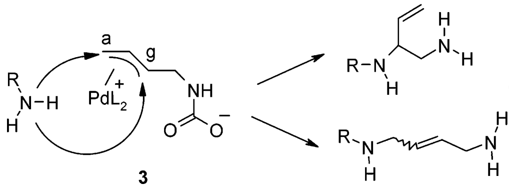
Results and Discussion

We briefly studied the solution polymerization of **1** using amine initiators to establish if **1** is an efficacious monomer for the ring-opening polymerization we intended to use for grafting to a surface. A model reaction was carried out at room temperature using 5 mol % isobutylamine initiator, 1 mol % Pd(dba)$_2$ and 4 mol % PPh$_3$ in a freshly distilled THF solvent (eq 2). The product polymer had poor solubility in solvents other than MeOH and MeOH/CHCl$_3$ mixtures. We were able to characterize this product in solution. However, we sometimes observed that if the polymer was isolated and thoroughly dried, it would not redissolve in any tested solvent including the original solvents MeOH and MeOH/CHCl$_3$. These characteristics were also described by the Suzuki group for the polymers they prepared by the chemistry shown in eq 1.[19]



(2)

The isolated polymer **2** was characterized by ^{1}H NMR, ^{13}C NMR, ^{1}H−^{1}H COSY, and FTIR spectroscopy. FTIR spectroscopy showed that the carbonyl stretch at 1738 cm^{-1} in the monomer **1** spectrum was absent in the polymer product. ^{1}H, ^{13}C, and ^{1}H−^{1}H COSY (correlated spectroscopy) NMR spectroscopy indicated a structure for the product **2** of the isobutylamine-initiated polymerization that is shown in eq 2. This product had a mixture of 1,4-diamino-2-butenyl and 3,4-diamino-1-butenyl subunits. The *E*:*Z* diastereomer ratio of the 1,4-diamino-2-butenyl subunits was not determined due to overlap of peaks in the ^{1}H NMR spectrum. This mixture of regioisomeric units in the polymer product **2** is a result of the attack of amine nucleophiles on either the electrophilic α or γ electrophilic carbons of the intermediate p-allylpalladium complex **3** (eq 3). ^{1}H NMR spectroscopy studies of **2** shows that the polymer isolated from the Pd(0) catalyzed polymerization of **1** initiated by 5 mol % isobutylamine has ca. 3:1 α:γ regioselectivity based on integration of the alkenyl peaks.



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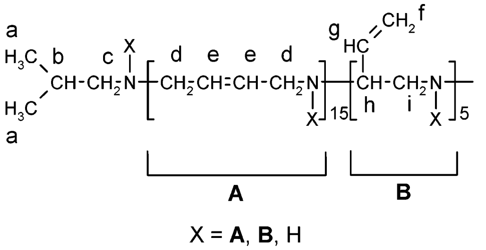
(3)

By using isobutylamine as the initiator, we were able to produce a hyperbranched polymer possessing −CH$_3$ groups from this initiator that were easily distinguishable from the protons on allylic positions. End group analysis using ^{1}H NMR spectroscopy was then used to determine the molecular weight of the hyperbranched polyamine polymer. The molecular weight was calculated from the integral ratios of the isobutylamine initiator −CH$_3$ peak at δ 0.87 and alkenyl peaks centered at δ 5.23 and δ 5.67. This ratio of the integrations for these peaks shows 18.73 monomer units for every isobutylamine unit which corresponds to a M_n of ca. 1360. This experimental M_n agrees with the theoretical M_n of ca. 1450, based on the starting 20:1 (monomer:initiator) reaction mixture. Analysis of the ^{1}H−^{1}H COSY NMR spectrum in Figure 1 shows the initiator **a** protons coupled to protons **b** that are in turn coupled to protons **c**. Unit **A** of the hyperbranched polymer has vinylic protons **e** that are coupled to the allylic protons **d**. The ^{1}H NMR spectrum shows two main peaks for the allylic protons **d** due to linear and branched portions of the polymer. The vinyl protons **f** of unit **B** are coupled to the proton **g** which is coupled to the allylic proton **h,** that is in turn coupled to protons **i**. The overlapping peaks **d** presumably represent allylic protons due to the linear, branched, and terminal butenyl groups. This NMR spectroscopy study allowed us to estimate the degree of polymerization using isobutylamine as an initiator. While we estimated the 3:1 ratio for regioisomers from these spectra, the complexity of the stereo- and microstructures for the unit structures **A** and **B** prevented the calculation for the degree of branching and the relative amounts of secondary and tertiary amine groups in **2**.


$$(\mathrm{H_3C})_2\mathrm{CH{-}CH_2{-}}\overset{X}{\mathrm{N}}\mathrm{{-}}\underbrace{\Big[\mathrm{CH_2CH{=}CH{-}CH_2{-}}\underset{X}{\mathrm{N}}\Big]_{15}}_{\mathbf{A}}\underbrace{\Big[\overset{\mathrm{HC{=}CH_2}}{\mathrm{CH}}\mathrm{{-}CH_2{-}}\underset{X}{\mathrm{N}}\Big]_{5}}_{\mathbf{B}}$$

These initial studies showed that Pd(0)-catalyzed polymerization of **1** initiated by an amine produced a hyperbranched polymer in direct analogy to the results of Suzuki.[18,19] However, our focus was the use of **1** in surface-initiated polymerization. To study the use of **1** in this application, we chose to study grafting chemistry of **1** initiated by aminosilane-functionalized silicon. Aminosilane functionalized surfaces are convenient chemical models of other amine-containing surfaces. Such surfaces are accessible by known chemistry from the native oxide layer of a silicon wafer using (aminopropyl)triethoxysilane as an aminating agent.

The general scheme used in our grafting studies is illustrated in Scheme 1. After an initial aminosilylation of the native oxide layer of a silicon wafer, the amine modified wafer was immersed in a degassed solution containing 0.66 M **1**, 0.013 M Pd(dba)$_2$, and 0.053 M triphenylphosphine at room temperature. After 12 h,

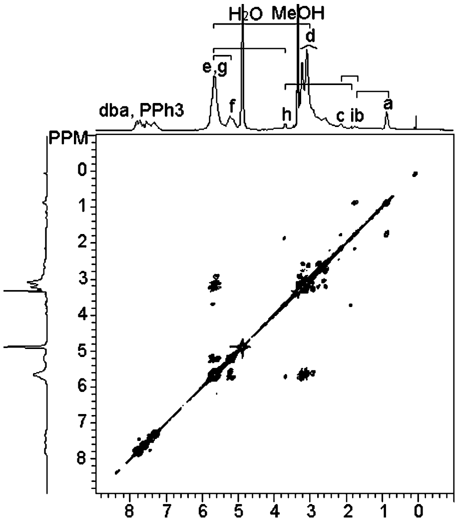
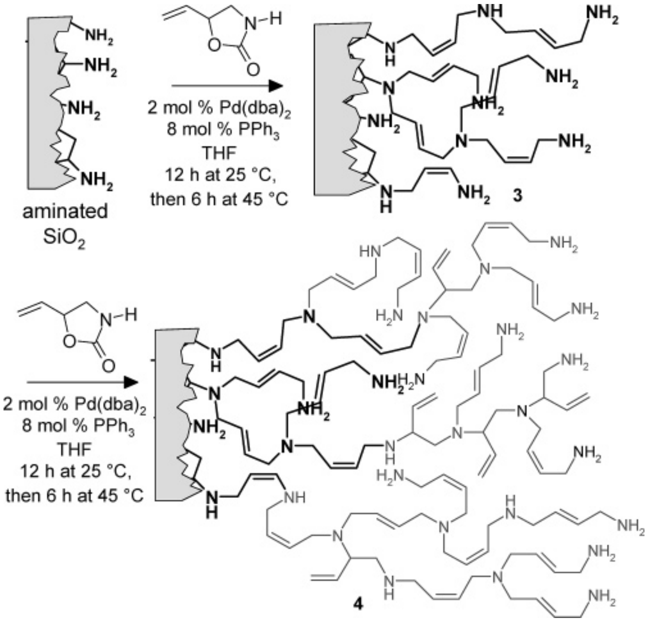


Figure 1. ^{1}H NMR spectrum of isobutylamine initiated VOX polymerization. The proton couplings determined by ^{1}H−^{1}H COSY NMR spectroscopy are depicted with brackets.

Scheme 1. Preparation of Hyperbranched Poly(1-aminobutdiene) Graft 4 Starting with an Aminated Silicon Wafer



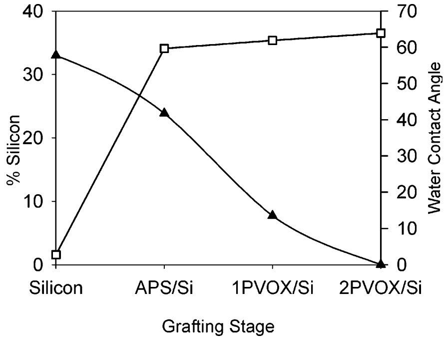


Figure 2. XPS spectroscopic analysis (▲) of the atom % Si through various grafting stages of VOX on aminosilated silicon contrasted with the advancing water contact angle (□) through various grafting stages of PVOX on aminosilated silicon.

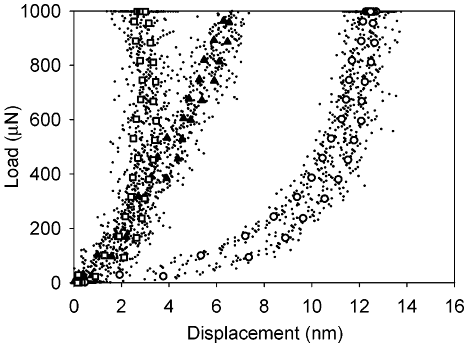


Figure 3. Load-displacement curves for (□) silicon (▲) (aminopropyl)triethoxysilane functionalized silicon (○) a PVOX graft on a silicon wafer after two cycles of grafting with Pd(0) and **1**. The symbols □, ▲, and ○ are averages of every 30 data points and were added for clarity.

Table 1. XPS Analysis Data and Water Contact Angle Data for PVOX Grafting on Aminosilylated Silicon

substrate	% Si	% N	% C	% O	Θ_a (deg)
Si	28.8		3.2	67.9	
APS/Si	23.9	3.7	31.8	40.6	60
1-PVOX/Si	7.7	15.4	62.7	14.2	62
2-PVOX/Si	0.0	15.0	74.8	10.2	64

the reaction mixture was heated to 45 °C for an additional 6 h. After grafting, the wafer was removed from the monomer solution, the wafer was washed first with THF and then with MeOH and finally sonicated in methanol to remove any ungrafted residue. The wafers were dried under a stream of N_2 and then analyzed by X-ray photoelectron spectroscopy (XPS). These analyses of the wafer after successive grafting stages show an increase in the atomic percent of N and C with a decrease in atomic percent concentration for the Si of the silicon wafer substrate (cf. Figure 2 and Table 1). For example, the aminosilane treated silicon wafer N peak intensity increased from 3.70 atom % to 15.36 atom % after the first grafting stage while the C peak intensity increased from 31.83 to 62.71 atom %. The Si peak intensity decreased from 23.86 to 7.70 atom %. The amount of grafting varied depending on how much catalyst was used and on whether the catalyst or the graft reaction mixture had been exposed to oxygen. Reactions where the grafting solution was exposed to oxygen after the initial room-temperature portion of the grafting produced Pd(0) and a higher residual Si peak in the product's XPS spectrum. Reactions where more catalyst was added had increased amounts of grafting with a lower Si at. % in the product's XPS spectrum. Reactions without rigorous oxygen removal from solvents failed completely. Because of the oxygen-sensitivity of the catalyst, the only way we were able to obtain complete grafting (i.e., to obtain a product with no detectable Si in the product) was to use a second grafting step. Table 1 shows the result of a second grafting stage (using the same conditions of the first stage) where the Si peak intensity decreased to 0 atom %. Contact angle analysis shows that these grafted surfaces were more hydrophobic than the unmodified silicon though the water contact angle on the hyperbranched surfaces was not appreciably different from the (aminopropyl)triethoxysilane-treated surface. Other (aminopropyl)triethoxysilane functionalized substrates including glass and silica gel were used in this chemistry as well. In these cases too the grafting coverage was such that there was a residual Si peak in the XPS spectrum. Typical atom % Si values in these cases after two grafting stages on an aminosilated glass slide and aminosilated silica gel were 3.2 and 6.4 atom %, respectfully.

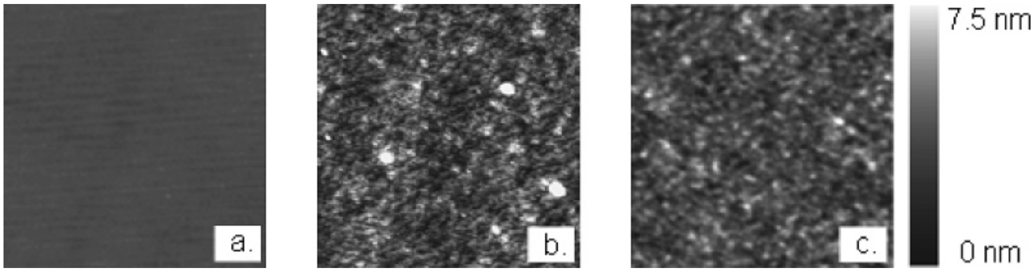
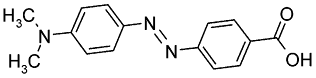


Figure 4. 2 × 2 μm TM-AFM images of (a) silicon, (b) PVOX graft on Si, and (c) 3-PAA graft on Au.[21]

The success of grafting was also assayed by examining the surface mechanical properties. This assay was carried out using a nanoindenter. The load-displacement curves for silicon, aminated-silicon, and 2-PVOX-silicon wafers are shown in Figure 3. These curves show that after the surface is functionalized, the displacement depth increases. The relatively soft PVOX grafted silicon wafer has a load-displacement curve that is significantly different either from the silicon wafer and (aminopropyl)triethoxysilane functionalized wafer. Similar graft polymerizations carried out on glass substrates were also studied with a nanoindenter but these studies were frustrated by insufficient and/or irregular grafting coverage and by the irregular surface of these substrates.

The surface roughness of these grafts was measured by tapping-mode atomic force microscopy (TM-AFM). The very smooth silicon single crystal substrate had a root-mean-square (rms) roughness of 0.15 nm. After functionalizing this silicon substrate with (aminopropyl)triethoxysilane the rms roughness increased to 0.5 nm. These roughness measurements of the silicon wafer and (aminopropyl)triethoxysilane functionalized silicon wafer are both similar to recently reported results.[21] After one PVOX grafting stage on (aminopropyl)triethoxysilane functionalized silicon wafer, the rms surface roughness increased to 0.9 nm. A second grafting stage increased the rms surface roughness to 1.3 nm. The roughness increased with each PVOX grafting stage with a very smooth silicon substrate. This behavior was also seen with hyperbranched PAA grafts on an initially smooth gold substrate.[22] For example, a single crystal gold substrate which had an rms surface roughness of 0.2 nm had its roughness increase to 0.8 nm after three poly(acrylic acid) grafting stages. Figure 4 shows tapping mode atomic force microscopy images that compare a very smooth silicon substrate, a PVOX graft and a previously reported hyperbranched poly(acrylic acid) (PAA) grafts on a smooth Au(111) single crystal.[22]

The polyamine grafts prepared using the chemistry in Scheme 1 behave as a basic surface as expected. The simplest demonstration of this was an experiment where the hyperbranched polyamine graft on silica gel was treated with the acidic dye **5**.[23] This produced a red surface whose color was stable to solvent washing but removable after dilute acid treatment. A control experiment using an (aminopropyl)triethoxysilane treated surface and this same azo dye showed no visual surface dyeing. A control experiment using the same azo dye and commercially available poly(ethylene imine)-grafted silica gel showed a slight yellowing of the product silica gel with this same dye.

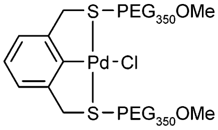


5

Grafting of VOX to an amine functionalized surface generally produced a surface with some residual Si in XPS analyses. This was true if the starting surface was a silica wafer, silica gel, or glass. The amount of residual Si also varied from experiment to experiment The need for multiple grafting stages to produce a graft that completely covered the Si in as measured by XPS spectroscopy could be explained by incomplete functionalization with (aminopropyl)triethoxysilane. However, we believe that the problems in this reaction stem from the fact that this grafting chemistry requires a biomolecular reaction between a surface and an air-sensitive palladium(0) catalyst or an intermediate derived from this catalyst because residual Si is seen in XPS spectra of products derived from various substrates aminated by various aminopropylsilyation protocols. Adventitious oxidation of phosphine ligands of the in situ formed Pd(0)-phosphine catalyst leads to formation of Pd(0) colloids (Pd black). Even if such colloids have some reactivity in allylic substitution chemistry of homogeneous substrates,[24] such colloids likely would be inactive in reactions with a heterogeneous substrate like those used here.

Several control experiments were used to show that these reactions are analogous to the solution chemistry of phosphine-ligated Pd(0) complexes and allylic acetates. No reaction is expected between a simple amine and a carbamate like **1**. Palladium(0) is necessary for this chemistry to occur. A grafting reaction in which no palladium was present was, not surprisingly, ineffective. Also, grafting was ineffective when oxygen was inadvertently introduced into the reaction mixture as judged by the rapid precipitation of palladium black. Allylic substitution using Pd(0) catalysts is inhibited by the presence of excess phosphine. We carried out a reaction similar to that shown in Scheme 1 using a Pd(0) catalyst but with a 4-fold excess of triphenylphosphine. Grafting was ineffective. These control experiments are consistent with the notion that Pd catalysis is required for these grafting reactions to occur.

An effort to circumvent the oxygen-reactivity of the Pd-complexes used in Scheme 1 was unsuccessful. We attempted a polymerization of **1** using an air stable SCS−Pd(II) complex **6** as the source of Pd.[25,26] In an attempted polymerizations of VOX with 1 mol % of **6** under conditions where a similar concentration of $Pd(PPh_3)_4$ would have yielded polymer, no polymer formed after 72 h.



6

Experimental Section

General Procedures. Toluene and THF were obtained from Aldrich and were distilled under N_2 from a sodium-benzophenone mixture before use. (Aminopropyl)triethoxysilane was obtained from Gelest or Aldrich (99%) and was distilled under reduced pressure before use. Benzylamine (99%), isobutylamine (99%), triphenylphosphine (99%) and dibenzylideneacetone (99%) were obtained from Aldrich. The $Pd(dba)_2$ was prepared according to a literature procedure.[27] The monomer 5-vinyl-2-oxazolidinone was a gift from the Eastman Chemical Co. It was analyzed before use by ^{1}H NMR spectroscopy and GC and had no detectable impurities in either analysis. The 4" silicon substrates were obtained from University Wafer and cut into 1 × 3 cm pieces. Tapping-mode atomic force microscopy was performed using a Digital Instruments Nanoscope IIIa (Santa Barbara, CA) equipped with a "j" scanner. Etched silicon tapping-mode cantilevers had resonant frequencies between 260 and 280 kHz, and tip apex radii between 5 and 10 nm. Images were acquired with 512 × 512 pixels at 1.0 Hz using minimal engagement force. Images were flattened and plane-fit using Digital Instruments software. Nanoindentation experiments were performed using a Hysitron Triboindenter (Minneapolis, MN) fitted with a 10 μm radius, cono-spherical diamond indenter. The instrument consists of a three-plate capacitive transducer that is used as both the actuator and the sensor of the instrument mounted onto a piezoelectric tube scanner. Load-controlled force vs distance plots were obtained by first bringing the tip into minimal contact with the surface, allowing transducer and piezoelectric drift to settle, and then running a loading/unloading cycle. Loading and unloading rates were 3.33 μN/s. X-ray photoelectron spectra were obtained on a Kratos Axis Ultra XPS (Manchester, U.K.) using a monochromatic Al Kα source (400 W) in a UHV environment (ca. 5×10^{-9} Torr). During acquisition, surfaces were kept from charging by the application of low energy electrons. Surface elemental composition was determined by normalized integration of the resulting peaks using Kratos software. ^{1}H, ^{13}C, and ^{1}H$-$^{1}H COSY NMR spectroscopy experiments were carried out using Mercury 300, Unity 300, or Unity 500 spectrometers.

Solution Polymerization of 5-Vinyl-2-oxazolidinone. A solution of **1** (904 mg, 8 mmol) dissolved in 4 mL of distilled THF was first added to a N_2-filled 40 mL centrifuge tube. This solution was then degassed by three freeze/pump/thaw cycles. A second N_2-filled centrifuge tube containing the catalyst mixture of $Pd(dba)_2$ (44.8 mg, 0.08 mmol) and triphenylphosphine (84 mg, 0.32 mmol) in 6 mL of distilled THF was also degassed by three freeze/pump/thaw cycles. The catalyst mixture was transferred to the monomer solution by forced siphon using a cannula. Then a degassed solution of isobutylamine (29.3 mg, 0.4 mmol) initiator in 2 mL of THF was added to the reaction mixture by forced siphon. The polymer precipitated as the polymerization progressed. Typically a precipitate of the product polymer began to appear after 1 h. The reaction mixture was allowed to stir for a total of 48 h at room temperature before the crude product polymer precipitate was isolated by centrifugation. The product polymer (0.44 g) was isolated by dissolving this precipitate in 10 mL of methanol and recovered by precipitation with 100 mL of ether. The ^{1}H NMR spectra indicated that this crude product contained some PPh_3 and dibenzylideneacetone impurities that were not removed by solvent precipitation. The product polymer was triturated with DMF for 48 h in an attempt to remove these impurities. The molecular weight was calculated from the integral ratios of the isobutylamine initiator $-CH_3$ peak at δ 0.87 and alkenyl peaks centered at δ 5.23 and δ 5.67. This ratio of the integrations for these peaks shows 18.73 monomer units for every isobutylamine unit which corresponds to a M_n of ca. 1360. The proton spectrum consists of complex multiplets, the center peak assignments are listed. Figure 1 shows the ^{1}H$-$^{1}H COSY NMR spectrum with the coupled protons in brackets: ^{1}H NMR (CD_3OD) δ 0.87 ($-CH_3$ groups of the isobutyl initiator), 1.85, 2.14, 2.58, 3.09, 3.22, 3.69, 5.23 (vinyl C$-$H), 5.67 (vinyl C$-$H); ^{13}C NMR (CD_3OD) δ 21.63, 43.41, 44.09, 44.78, 46.40, 47.91, 51.32 (br), 55.89 (br), 118.91 (br), 127.91, 128.81, 129.88, 131.02, 132.96, 133.38, 135.11 (br), 136.39; FT-IR (KBr, cm^{-1}) 3430 (br, N$-$H), 2937 (br, C$-$H), 1645 (br, C=C), 1449, 1377, 1127.

A benzylamine-initiated polymerization of 5-vinyl-2-oxazolidinone was also successfully carried out. Although the spectra of this product were not as extensively analyzed, the ^{1}H and ^{13}C NMR of this product were qualitatively similar to the spectra of the isobutylamine derived product (except for the initiator groups). Overlap of the vinyl protons of the product with the aryl protons of the benzylamine precluded end group analysis in this case.

(Aminopropyl)triethoxysilane Modification of Si Substrates. Several procedures were used. As in prior work,[28] we used an established procedure for surface amination.[29,30] This chemistry yielded a surface with 28.1 atom % Si, 29.7 atom % C, and 4.9 atom % N. While grafting of **1** occurred with wafers so modified (or with glass or silica gel materials aminosilyated by other procedures),[31,32] the results in Table 1 and the nanoindenter studies all used silica wafers that had been aminopropylsilylated after cleaning with a series of washing and baking steps. First, the wafer was soaked in concentrated H_2SO_4 for 12 h. This wafer was then rinsed with 18.2 MΩ Millipore water and placed in a 1000 °F furnace for 12 h. This cleaned silicon wafer was then immersed in a toluene solution containing 10% (v/v) 3-aminopropyl)triethoxysilane(APS). This mixture was stirred under N_2 for 12 h at 110 °C. After cooling to room temperature, the wafer was removed and washed with copious amounts of THF, ethanol, and methanol and then dried under a stream of N_2: XPS analysis of the clean silicon wafer showed 28.8 atom % Si, 3.2 atom % C, and 67.9 atom % O. After the reaction with APS, XPS analysis showed 23.9 atom % Si, 3.7 atom % N, 31.8 atom % C, and 40.6 atom % O. The clean silicon wafer did not have a measurable contact angle. After the APS reaction the contact angle was measured to be 60 ± 3°.

Typical Grafting Procedure. Grafting to silicon substrates was achieved by immersing an aminated wafer in a 40 mL centrifuge tube containing the solution of **1** (452 mg, 4 mmol) in 2 mL of distilled THF under N_2. The catalyst mixture of $Pd(dba)_2$ (44.8 mg, 0.08 mmol) and triphenylphosphine (84 mg, 0.32 mmol) in 4 mL of distilled THF under N_2 was degassed using three freeze/pump/thaw cycles. This solution was transferred by forced siphon using a cannula into the centrifuge tube containing the slide and monomer solution. This mixture was degassed three more times and then warmed to room temperature and allowed to sit for 12 h. At this point, the reaction mixture was heated to 45 °C for an additional 6 h. After the wafer was removed from the reaction solution, the wafer was washed first with THF and then with methanol and finally further cleaned by sonication in methanol (5 min). The product silicon-supported thin film was analyzed by XPS and contact angle goniometry. Analysis of one grafting stage by XPS showed 7.7 atom % Si, 15.4 atom % N, 62.7 atom % C, and 14.2 atom % O. The contact angle after one grafting stage was measured to be 62 ± 3°. After a second grafting reaction XPS showed 0.0 atom % Si, 15.0 atom % N, 74.8 atom % C, and 10.2 atom % O. The contact angle after two grafting stages was measured to be 64 ± 3°.

Conclusion

The results above show that direct hyperbranched graft polymerization of a monomer like **1** produces hyperbranched graft aminated surfaces. The chemistry is complicated by the oxygen-sensitivity of the Pd(0) catalyst but is a general reaction leading to aminated surfaces that occurs under relatively mild conditions.

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