Biomass

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Polysilylether: A Degradable Polymer from Biorenewable Feedstocks

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Abstract: *The synthesis of polysilylethers (PSEs) using a monomer derived from a biorenewable feedstock is reported. The AB-type monomer was synthesized from undecenoic acid through hydrosilylation and reduction, and the polymerization was catalyzed by earth-abundant metal salts. High-molar-mass products were achieved, and the degree of polymerization was controlled by varying the amount of an AA-type monomer in the reaction. The PSEs possess good thermal stability and a low glass-transition temperature ($T_g \approx -67\,°C$). To demonstrate the utility of the PSEs, polyurethanes were synthesized from low-molar-mass hydroxy-telechelic PSEs.*

The global production of plastics reached 300 million metric tons in 2013.[1] The vast majority of these materials are sourced from non-renewable fossil fuels.[2] For many reasons, it is beneficial to develop polymer materials sourced from renewable feedstocks. Currently, several renewable polymers have been developed and commercialized, including poly(lactic acid) (PLA), poly(hydroxyalkanoate)s (PHA), polyamide 11, and bio-polyethylene. However, the total volume of biorenewable polymers represents a very small fraction of the global plastic production, and less than half of those materials are biodegradable.[2]

Issues concerning the disposal of plastics must also be addressed. The thermal, oxidative, and hydrolytic stability of most synthetic polymers leads to their accumulation in the biosphere. It is estimated that a quarter of plastic worldwide is disposed in landfills, and tens of millions of metric tons of plastics accumulate in the oceans, causing damage to aquatic ecosystems.[1] Thus, it is important to design, synthesize, and evaluate polymers that can be degraded under mild, ambient conditions into low-molecular-weight monomers or oligomers and can either be further metabolized by microorganisms or otherwise assimilated.[3] Usually, biodegradable polymers contain heteroatom linkages in the backbone (such as polyesters), allowing degradation through hydrolysis or enzymatic chain scission.

To develop new renewable and degradable polymers, we sought to incorporate Si–O linkages into the polymer backbone. Silyl ethers are common protecting groups used in organic synthesis and can be cleaved by hydrolysis under acidic or basic conditions to give the corresponding alcohols and siloxanes.[4–6] The rate of hydrolysis depends on the steric properties of the substituents on the silicon and carbon atoms α to the oxygen atom.[7] In addition, the relatively large Si–O and Si–C bond lengths can increase the flexibility of the polymer backbone, thus leading to low glass-transition temperatures, a property that is important for creating elastomers or tougheners for other plastic materials.[8,9]

Polymers containing either C–Si–O–C or C–O–Si–O–C linkages in the repeating unit have been synthesized by several methods: 1) uncatalyzed melt-condensation of aryl- or biaryldiols with dianilino- or diphenoxysilanes;[10–12] 2) reactions of dichlorosilanes with either bis(epoxide)s or bis(oxetane)s catalyzed by quaternary ammonium salts,[13–15] thus resulting in polymers with reactive pendant chloromethyl groups; 3) hydrosilylation of aliphatic and aromatic ketones or benzoquinones with hydrosilanes catalyzed by ruthenium and palladium complexes;[16–18] and 4) dehydrogenative coupling of alcohols with hydrosilanes catalyzed by palladium and rhodium complexes.[19,20] Polysilylethers (PSEs) bearing aryl and biaryl backbones are typically solids with softening temperatures above 50 and 150 °C, respectively,[10,11] whereas those bearing aliphatic backbones typically have glass-transition temperatures (T_g) below −80 °C.[16] These studies have shown, as expected from the chemistry of silyl protective groups, that PSEs synthesized from secondary alcohols or from silanes bearing bulky groups (e.g., Ph)[15,20] are much more resistant to either hydrolysis or methanolysis than are PSEs made from either primary alcohols or from silanes bearing unhindered groups (e.g., Me).[16,20] Most recently, polymers containing C–O–Si–O–C linkages were synthesized through silicon acetal metathesis polymerization catalyzed by a strong acid.[21] The methanol byproduct was actively removed during the reaction to drive the equilibrium to the polymer product.[21]

For several reasons, we considered undecenoic acid derivatives to be a desirable starting material to prepare polysilylethers (PSE). Undecenoic acid is derived from pyrolysis of rincinoleic acid, a principal component of castor oil.[22] Undecenoic acid contains a terminal alkene and a terminal carboxylic acid which allow sequential functionalization to construct an AB-type bifunctional monomers.[23] Once functionalized on both termini, the molecule contains 11 CH_2 units, which should further increase the flexibility of the resulting polymer chain.

We report the synthesis of a novel, bifunctional monomer containing Si–H and OH functionalities from an undecenoic acid derivative and polymerization of this monomer to afford PSEs with controlled molar mass. The PSEs undergo controlled degradation in neutral to moderately acidic (pH 2) aqueous media and are suitable for constructing polyur-

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ethanes (PU) using PSEs as a macromolecular diol creating soft segments.

We envisioned a method to combine commodity silanes with undecenol by hydrosilylation of the alkene, and subsequent polycondensation forming Si−O bonds. Although Si−O bonds can be formed through the direct reaction of Si−Cl and R−OH moieties, this reaction requires a stoichiometric amount of base and separation of the stoichiometric corresponding salt byproduct. In addition, a monomer containing a Si−Cl moiety will be sensitive to moisture. Thus, we sought to use the catalytic dehydrogenative condensation of Si−H and OH groups[24–26] as an alternative strategy to form the Si−O bonds. The advantage of this strategy is that Si−H bonds are hydrolytically stable and do not readily react with OH groups in the absence of a catalyst. In addition, the only byproduct of this coupling process is H_2, which is easily removed.

To synthesize a bifunctional molecule, containing one Si−H and one OH moiety, from undecenoic acid, we conducted the hydrosilylation of methyl 10-undecenoate with Me_2SiClH catalyzed by 10 ppm of Karstedt's catalyst[27] (Figure 1). The Si−Cl moiety was used as a masked Si−H

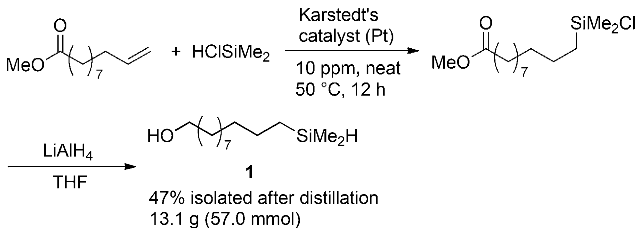


Figure 1. Synthesis of the bifunctional monomer **1**. THF = tetrahydrofuran.

group because Me_2SiH_2 is a catalyst poison.[28–30] One-pot, consecutive reduction of both the Si−Cl and the ester groups with $LiAlH_4$ (which ensures that the Si−Cl and OH moieties are not present in the same pot because the Si−Cl reduction is much faster than that of the ester reduction) furnished the novel bifunctional monomer **1** on a decagram scale. The monomer was distilled to obtain material with a purity (99.5% by GC analysis) suitable for synthesis of high-molar-mass polymers by step-growth polymerization.

Several methods for the dehydrogenative silylation of alcohols are known, including reactions catalyzed by transition-metal complexes[20,31] and by boranes.[24] We first attempted the dehydrogenative polymerization of **1** with $[\{Ir(coe)_2Cl\}_2]$ as the catalyst, based on prior work on the iridium-catalyzed dehydrogenative silylation of alcohols by Simmons and Hartwig.[31] However, polymerization of **1** catalyzed by $[\{Ir(coe)_2Cl\}_2]$ at temperatures ranging from 20 to 80 °C led to insoluble products (Figure 2). This material was tentatively assigned to be a cross-linked polymer because the reaction of a hydrosilane with an iridium precursor lacking strongly coordinating ligands has been shown to form a silane-bridged dimeric iridium species containing multiple silyl groups bound to iridium.[32,33] Similarly, polymerization conducted with $[\{Ru(p\text{-cymene})Cl_2\}_2]$ as the catalyst led to an

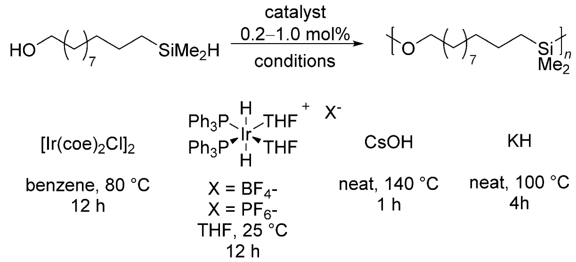


Figure 2. Dehydrogenative polymerization of **1** by various catalysts. coe = cyclooctene.

insoluble material. Thus, we conducted the polymerization with the more defined, single-site iridium catalysts reported by Luo and Crabtree.[34] However, the molar mass of the resulting polymeric products was relatively low.

Although many other transition metals could be evaluated for this process, these iridium and ruthenium catalysts are among the most active for dehydrogenative silylation. Thus, we investigated reactions catalyzed by alkali-metal alkoxides. The ring-opening polymerization of octamethyltetrasiloxane (D4) catalyzed by alkali-metal hydroxides[35] and the dehydrogenative silylation of alcohols catalyzed by strong inorganic bases are known.[36–39] Thus, we investigated the polymerization of neat **1** with CsOH (0.2-1 mol%) as the catalyst (Figure 2). The polymerization proceeded rapidly at 140 °C under these conditions to afford a transparent viscous oil. KH was also studied as the catalyst, and in this case the reaction proceeded at 100 °C with 1 mol% of KH. The NMR spectrum of the product consisted of well-resolved signals for the silicon methyl groups, the methylene group α to silicon, and the methylene groups α and β to the oxygen atom. Signals corresponding to the monomer were not observed. These data provided preliminary evidence for formation of the targeted polymer and high conversion of the monomer.

The functionality at the terminus of the polymer chains was deduced by analysis of the end groups (Figure 3). The

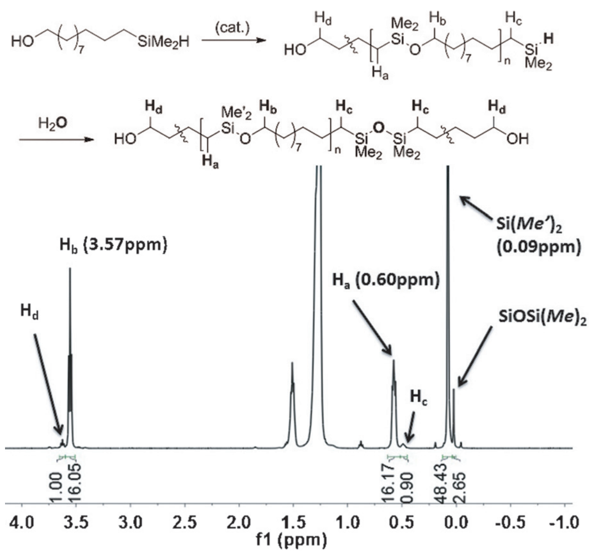


Figure 3. Detailed structure of the PSE with signals corresponding to the end groups labeled as H_d, H_c, and $SiOSi(Me)_2$.

^{1}H NMR spectrum of the polymer contained a triplet at $\delta=3.57$ ppm corresponding to the CH_2OSi group, a multiplet at $\delta=0.60$ ppm corresponding to the SiOCH_2 group, and a singlet at $\delta=0.09$ ppm corresponding to the Si(CH_3)$_2$. No signals from the Si–H functionality were observed, thus indicating complete reaction at these bonds. The ^{1}H NMR spectrum revealed a group of small triplets ($\delta=3.66$–3.60 ppm) that resonate 0.08 ppm downfield of the major CH_2OSi signal ($\delta=3.56$ ppm) of the polymer chain, a small multiplet ($\delta=0.51$ ppm) that resonates 0.09 ppm upfield of the major CH_2SiO signal ($\delta=0.60$ ppm), and a small singlet ($\delta=0.04$ ppm) that resonates 0.05 ppm upfield of the major Si(CH_3)$_2$ signal ($\delta=0.09$ ppm). Together, these signals indicate the presence of Si–O–Si linkages within the polymer chain. Assuming the Si–O–Si linkage results from reaction of two Si–H ends of a monomer with H_2O (most likely formed from reaction of CsOH with the OH groups of the monomer), an excess of OH groups would be present in the reaction. Thus, both ends of the polymer should be terminated by OH groups.

This hypothesis is supported by comparing the chemical shifts of the aforementioned protons to those of the model compound **2** (Figure 4). The Si(CH_3)$_2$ and CH_2SiO signals of the proposed Si–O–Si linkages in the polymer overlap with those of **2**, and the signal from the CH_2OH unit in the

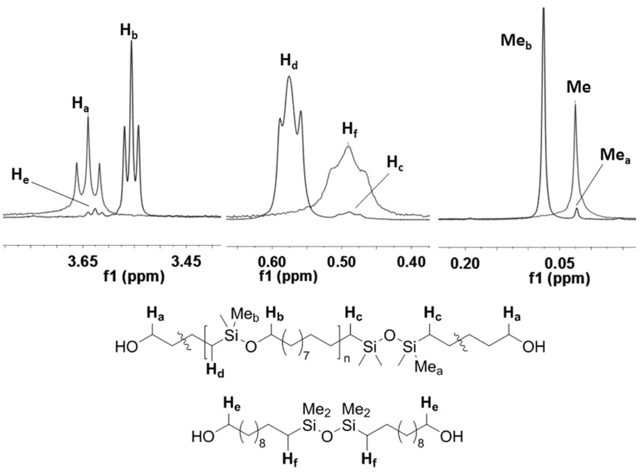


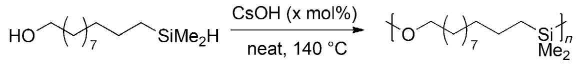
Figure 4. Comparison of the ^{1}H NMR spectrum of PSE to that of the model compound **2**.

proposed OH end groups in the polymer overlap with those of the CH_2OH end of **2**. Consistent with this assignment, the ratio of the integrations between the major and the minor signals resulting from the CH_2O, CH_2SiO, and Si(CH_3)$_2$ groups are consistent with this assignment.

The molar mass of the polymer can be estimated from the ratio of the CH_2OH and CH_2OSi by NMR spectroscopy ($M_n=21$k; see the Supporting Information) assuming exactly two end groups per chain. These data agree with the molar mass measured by light scattering size exclusion chromatography analysis ($M_n=23$ kg mol^{-1}; Table 1).

Because H_2O can effectively act as a dihydroxy AA-type monomer which introduces a stoichiometric imbalance during

Table 1: The effect of catalyst loading on the molar mass of the polymers.[a]



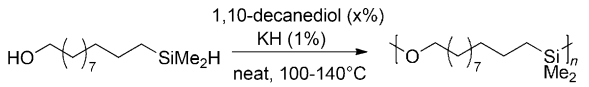
Entry	x	M_n[b]	M_n[c]	M_w[c]	$Đ$[c]	M_n[d]	M_w[d]	$Đ$[d]
1	0.2	30	49	85	1.74	37	65	1.72
2	0.5	21	38	63	1.65	23	40	1.69
3	1	16	24	43	1.80	17	29	1.73
4	2.5	7	9	16	1.88	8	11	1.40

[a] dn/dc = 0.049. dn/dc of the polymer was determined using a sample with a M_n of 10 kg mol^{-1} (by SEC). Molar masses are in kg mol^{-1}. [b] Determined by NMR spectroscopy. [c] Determined by SEC with RI. [d] Determined by SEC with LS.

polymerization,[40] we hypothesized that the degree of polymerization could be controlled by varying the amount of catalyst (and thus H_2O) in the system.[41] To test this hypothesis, we conducted the polymerization with 0.5–2.5% CsOH and examined the molar masses by both NMR analysis and by SEC equipped with a differential refractive index (RI) and light scattering (LS) detectors. Indeed, the molar masses of the polymer formed from reactions conducted with larger quantities of H_2O (from CsOH) were lower than those from reactions with smaller quantities of H_2O (Table 1).

To avoid side reactions associated with excess, unquenched hydroxide catalysts, we conducted the polymerization with a constant (1 mol%) amount of KH and controlled the molar mass by adding various amounts of AA-type monomer 1,10-decanediol as opposed to various amounts of CsOH.[42] The molar mass of the polymer, formed from a series of polymerizations with 1–8 mol% 1,10-decanediol, decreased with increased loading of 1,10-decanediol (Table 2).

Table 2: The effect of 1,10-decanediol on the molar masses of PSE.[a]



Entry	x	M_n[b]	M_n[c]	M_w[c]	$Đ$[c]	M_n[d]	M_w[d]	$Đ$[d]
1	1	14	23	43	1.9	16	33	2.0
2	2	8.1	11	15	1.4	n.d.	n.d.	n.d.
3	4	4.9	5.6	9.0	1.6	n.d.	n.d.	n.d.
4	8	2.6	3.6	6.3	1.8	3.1	4.6	1.5

[a] Molar masses are in kg mol^{-1}. [b] Determined by NMR spectroscopy. [c] Determined by SEC with polystyrene standards. [d] Determined by SEC with light scattering. n.d. = not determined.

The PSEs produced by the based-catalyzed polymerization were, in general, colorless, viscous oils or soft solids, depending on the molar mass. Analysis of the PSE with an M_n value of about 23 kg mol^{-1} by thermogravimetric analysis showed that this material lost 1% of its weight at 244 °C and 5% of its weight at 278 °C. Thus, the PSEs are significantly more thermally stable than polysilicon acetals containing aliphatic backbones[21] but less stable than PSEs containing aromatic backbones.[10,17,20] The T_g of the polymer is −67 °C, and no significant melting or crystallization transitions were observed by differential scanning calorimetry.

Having designed the polysilylethers to undergo hydrolysis at the Si–O bonds, we tested the stability of the PSE materials toward mixtures of aqueous and organic solvents, and water alone under hydrolytic degradation conditions. Dissolution of a PSE sample ($M_n \approx 23\,\mathrm{kg\,mol^{-1}}$) in a common organic solvent, such as THF, followed by addition of an equal volume of neutral water led to complete degradation to **2** under these biphasic conditions after either 24 hours at 50 °C, or after 2 days at 23 °C. In addition, complete degradation of the same polymer at 50 °C occurred within 7 days in water at pH 2 and within 50 days at pH 4 to give **2** as a white foam in the aqueous layer, despite the low solubility of the starting polymer in water.[43] At room temperature, complete degradation at pH 2 occurred over 22 days. Degradation even occurred at neutral pH at 50 °C, and 10 % of the Si–O bonds hydrolyzed after 50 d (Figure 5).

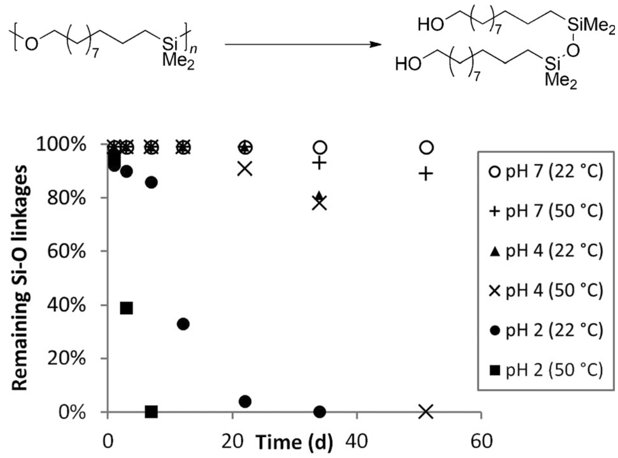


Figure 5. Degradation of PSE in water. Conversion of the silylether linkages as determined by NMR spectroscopy.

To exploit the low T_g value of the polysilylethers and the hydroxy termini, we synthesized polyurethanes from a hydroxy-telechelic PSE (ca. $3\,\mathrm{kg\,mol^{-1}}$) and a diisocyanate. The polymerization was conducted with methylene diphenyl diisocyanate (MDI) in THF at 65 °C for 4 hours with 2 mol % of $Sn(Oct)_2$ (relative to PSE, 1 mol % per OH end) as the catalyst. The formation of polyurethanes was evidenced by the NMR spectral data and SEC data of the material obtained after precipitation in MeCN to give a colorless and rubbery solid. The ^{1}H NMR spectrum of the polyurethane lacks the signal from the CH_2OH of the polymer initiator at $\delta = 3.62$–3.68 ppm. Instead, a triplet at $\delta = 4.13$ ppm was observed, thus corresponding to the $CH_2C(O)$ units at the carbamate linkages (see the Supporting Information). Comparison of the SEC traces of the polysilylether and the material formed after reaction with MDI indicates that the molar mass increased significantly (Figure 6). The M_n and M_w values, relative to polystyrene standards, were $29\,\mathrm{kg\,mol^{-1}}$ and $85\,\mathrm{kg\,mol^{-1}}$, respectively. The relatively large dispersity ($Đ = 2.94$) results from tailing of the peak at higher retention time

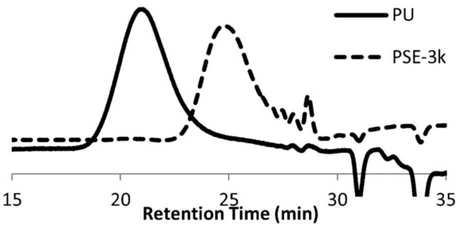


Figure 6. Overlay of the SEC traces of PU (solid line) and PSE (dashed line).

than that of the main peak (Figure 6, solid line). This lower-molecular-weight material most likely corresponds to a small amount of PSEs lacking hydroxy end groups. The M_n and M_w determined by light scattering are $45\,\mathrm{kg\,mol^{-1}}$ and $70\,\mathrm{kg\,mol^{-1}}$, respectively. The polymer exhibited good thermal stability (1 % weight loss at 209 °C and 5 % weight loss at 309 °C) and a glass transition at −68 °C.

In conclusion, we have synthesized a novel polysilylether which is sourced from a renewable feedstock and can be hydrolyzed under mild reaction conditions. The molar mass of the polymer can be controlled by varying the amount of AA-type monomer in the reaction system. In addition, we have synthesized a polyurethane from methylene diphenyl diisocyanate (MDI) and a dihydroxy-telechelic polysilylether. Further studies on the relationship between the length of the PSE and the physical and mechanical properties of the resulting polyurethane, and further studies on synthesizing additional copolymers with PSE structures are underway.

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