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Synthesis and Characterization of Degradable Poly(silyl ester)s

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ABSTRACT: Polymers containing labile silyl ester bonds along the backbone were synthesized via a transsilylation ester interchange reaction. The condensation of the bis(trimethylsilyl) esters of adipic acid and sebacic acid with several bis(silyl chloride)s gave trimethylsilyl chloride as the condensate and formed the new silyl ester bonds composing the polymer backbones. Alteration of the degradation properties of the poly(silyl ester)s was demonstrated with the synthesis of nine polymers consisting of three series with variation in the silicon side chain substituents, the backbone composition adjacent to the silicon atoms, or the backbone composition adjacent to the carbonyl moieties. Characterization of the poly(silyl ester)s included infrared spectroscopy, ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies, size exclusion chromatography (SEC) (typical molecular weights ranged from 2000 to 10 000), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The degradative properties of the polymers were evaluated by ^{29}Si NMR, and molecular weight loss was evaluated by GPC. Increased steric bulk and decreased electronegativity of the substituents attached to the silicon atoms resulted in decreased monomer reactivity and increased degradation times for the polymers. Hydrolysis of the polymers in solution gave small molecules while condensation of the disilanol degradation products occurred in the solid-state degradations to give polysiloxanes.

Introduction

Degradable polymers have received considerable interest for medical[1] and environmental[2] purposes because they can be constructed to possess the requisite physical and mechanical properties to perform a given function and later break down into biologically or environmentally resorbable small-molecule byproducts. Efforts have primarily been directed toward the development and application of poly(lactic acid), poly(glycolic acid), their copolymers, and other aliphatic polyesters.[3−7] More recently, the side-group chemistry of degradable polymers has been addressed,[8,9] in order to create functional materials that have the ability to bind to specific sites, carry drugs via covalent bonds, and so forth.

The stability or rate and mechanism of degradation are perhaps the most important parameters governing the applicability of degradable polymers, which requires accurate control over the reactivity of the bonds along the polymer backbone. Although modification of the backbone composition of polyesters affects the properties of the polymers, which can affect the hydrolytic stability (e.g. poly(glycolic acid) degrades more rapidly than poly(lactic acid)), the range of stabilities toward hydrolytic degradation available to aliphatic polyesters is limited. Anhydride,[10−12] ortho ester,[13−15] organophosphazene,[16−18] and silazane[19] linkages have also been investigated as labile bonds which have been incorporated into polymers to broaden the range of stabilities possible for polymeric materials.

The reactivity of a silyl ester linkage is highly dependent upon the steric and electronic properties of the substituents attached to the silicon. Nucleophilic attack on acyloxysilane groups can occur at both the silicon atom and the carbonyl carbon.[20,21] As substituents with increasing steric bulk or increasing electron-donating capabilities are attached to the silicon, an increasing amount of attack occurs at the carbonyl and the silyl ester stability approaches that of an ester functionality.

Silyl esters have been used as side groups for protection of carboxylic acid functionalities during anionic polymerization,[22−25] and the variable reactivity of the silyl ester bond has been used in a chemically amplified resist material.[26] However, the incorporation of acyloxysilane groups along a polymer backbone has only recently been achieved. Poly(silyl ester)s were reported as a new class of degradable polymers with variable and predictable degradation behavior.[27,28] As the steric bulk of the side-chain silicon substituents increased, the rate of nucleophilic attack decreased. Although a range of stabilities was demonstrated for the poly(silyl ester)s, each of the polymers studied were cleaved within 1 week upon reaction of the polymers as solutions in tetrahydrofuran with water, methanol, and *tert*-butanol added. In order to improve the hydrolytic stability of poly(silyl ester)s and also to investigate the effects of the main-chain substitutions, further modifications to the polymer composition have now been studied. Herein we report the synthesis, characterization, and degradation of several poly(silyl ester)s bearing substitution with groups of different steric and electronic properties on the silicon, and having varying backbone composition. Comparison is made between these polymers and the previously reported polymers, which results in varying effects being observed for the reactivity of the silyl ester linkage and therefore varying degrees of degradability.

Results and Discussion

Silyl esters are well-known as protecting groups for carboxylic acids, and several routes toward their preparation have been reported.[29,30] However, the conventional methods for the syntheses of silyl esters proved to be ineffective for polymer formation. For example, reaction of sebacic acid with dichlorodimethyl silane or 1,3-dichlorotetramethyldisiloxane in the presence of imidazole in *N*,*N*-dimethylformamide (DMF) at 50 °C gave only oligomeric products, even though these conditions are reported[31] to be efficient for sterically hindered chlorosilanes. The condensation of the disodium salt

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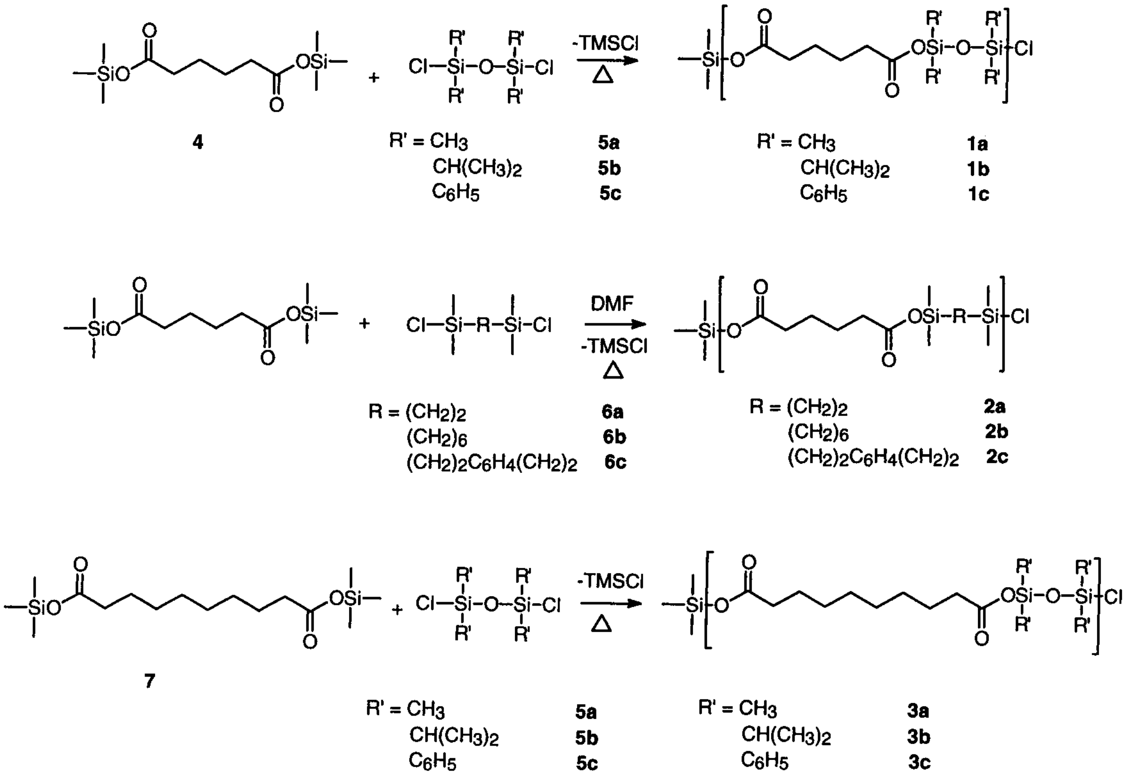
Scheme 1. Formation of Poly(silyl ester)s via Transsilylation Reactions



of sebacic acid with the above difunctional chlorosilanes also lead to oligomers. In both cases, large amounts of salt byproduct appeared to impede polymer formation. Therefore, amino silanes were employed as the comonomer units, to yield volatile byproducts. The condensation of sebacic acid with bis(dimethylamino)dimethylsilane initially gave poly(silyl ester)s of low molecular weight, which decomposed over the course of the polymerization to yield high-molecular-weight ($M_w \sim$ 100 000) polymers that were visible by viscometry detection (connected in-line with the gel permeation chromatography system) but not visible in the refractive index detector. ^{29}Si NMR confirmed that the polymer obtained was poly(dimethylsiloxane) and not the desired silyl ester polymer. Further analysis of the product mixture indicated that the byproduct, dimethylamine, attacked at the carbonyl carbon of the silyl ester bonds to produce amides and silanols. The silanols then condensed to yield the high-molecular-weight polysiloxane. Attempts to avoid the degradation of the polymer during synthesis included both the use of bis(diethylamino)dimethylsilane, to give a more sterically hindered diethylamine condensate, and the use of 1,1,3,3,5,5-hexamethylcyclotrisiloxane to increase the volatility of the byproduct amine. The bis(diethylamino)dimethylsilane underwent the same type of side reactions as the bis(dimethylamino)dimethylsilane had. Ring opening of the 1,1,3,3,5,5-hexamethyltrisiloxane did occur, but difficulties were experienced in the exchange of the silazane linkages for silyl ester bonds, and the complete exchange was not accomplished.

Therefore, the preparation of poly(silyl ester)s was afforded through a transsilylation reaction,[32,33] involving the condensation of a silyl chloride with a trimethylsilyl ester (Scheme 1). This reaction is very practical for polymer synthesis; the monomers used are readily purified, no solvent is needed and relatively low temperatures can be used for the polymerizations, the trimethylsilyl chloride byproduct is volatile and its reaction with the growing polymer chain is nonterminating, the reaction can be driven to completion, and when necessary only a simple catalyst is needed to allow the reaction to occur. In preliminary studies of the use of a transsilylation reaction for polymer synthesis, it was found that the necessity of a catalyst depends on the electronic properties of the silyl chloride monomer. With less reactive chlorosilanes (e.g., trialkyl substituted), a small molar percent of *N*,*N*-dimethylformamide (DMF) was found to be an effective catalyst for propagation of the reaction.[32]

The nine poly(silyl ester)s reported herein vary in both the substituents attached to the silicon atoms and the composition of the polymer backbone and are divided into three series, **1a**–**c**, **2a**–**c**, and **3a**–**c** (Scheme 1). All of the polymers were formed from the reaction of AA and BB type monomers, composed of bis(trimethylsilyl) esters and bis(silyl chloride) compounds. Initially, polymers **1a**–**c** were prepared by reaction of bis(trimethylsilyl) adipate (**4**) with 1,1,3,3-tetramethyldisiloxane, 1,1,3,3-tetraisoproyldisiloxane, and 1,1,3,3-tetraphenyldisiloxane (**5a**–**c**), respectively.[27,28] Degradation studies revealed that the substituents on the silicon atom resulted in variation of the rates of cleavage of the polymers by reaction with water, methanol, or *tert*-butanol. As the steric hindrance around the silicon atom increased, the rate of cleavage decreased.

Additionally, the largest nucleophile, *tert*-butanol, reacted most slowly with each of the poly(silyl ester)s. Because the electronic character of the silicon atom affects the susceptibility toward attack by a nucleophile, polymers **2a**–**c** were then prepared from the condensation of bis(trimethylsilyl) adipate with 1,2-bis(chlo-

Table 1. Characterization Data of Poly(silyl ester)s

polymer	M_w	M_w/M_n	DP_w	T_g (°C)	^{29}Si NMR δ (ppm)
1a	2850	2.2	10	−56	−7.48
1b	2700	1.7	6.9	−84	−11.38
1c	2650	1.9	5.0	3	−36.99
2a	3360	2.1	12	−56	23.84
2b	9760	3.9	34	−62	23.48
2c	8560	3.4	22	−37	23.09, 20.69
3a	2400	2.3	7.2	−77	−7.46
3b	3220	1.9	7.2	−85	−11.35
3c	2040	1.8	3.5	−6	−37.09

rodimethylsilyl)ethane (**6a**), 1,6-bis(chlorodimethylsilyl)hexane (**6b**), or bis((chlorodimethylsilyl)ethyl)benzene (**6c**). These polymers contain trialkyl-substituted silyl ester groups, and the effects from the replacement of the electronegative oxygen atom are discussed below. The extension of the alkyl spacers between the carbonyl groups was also investigated through the preparation of **3a**−**c**, from the tetrasubstituted-dichlorodisiloxane monomers (**5a**−**c**) and bis(trimethylsilyl) sebacate (**7**), as a means to alter the relative hydrophobicity in comparison to that of the initial materials (**1a**−**c**).

The polymerizations were all performed without the addition of solvent, and in the reactions to form **2a**−**c**, 1−5 mol % of DMF was added as a catalyst to the reaction mixture. The reaction mixtures were heated at approximately 100 °C under an argon atmosphere for 5−15 days. In all cases, the polymerizations were monitored by both ^{29}Si NMR and size exclusion chromatography (SEC), as both the disappearance of the monomers and the formation of the poly(silyl ester) backbone could be observed. The conversion of the chlorosilane monomers to silyl esters was observed by upfield shifts in the resonances for the silicon atoms by ^{29}Si NMR. In addition, the formation of TMSCl condensate was seen by the appearance of a ^{29}Si resonance at 31 ppm. Polymer growth was monitored by SEC. Typical molecular weights (M_w) of the polymers varied from about 2000 to 10 000, with the less sterically hindered monomers (i.e. those with methyl groups attached to the silicon) forming polymers under milder conditions (see Experimental Section) and having higher degrees of polymerization (Table 1). As is expected for condensation polymerizations, the molecular weight distributions (M_w/M_n) increased with increasing molecular weight.

The resulting polymers were each characterized by NMR (^{1}H, ^{13}C, and ^{29}Si), infrared spectroscopy (IR), SEC, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). In the infrared spectra of each of the polymers, a strong absorption for the carbonyl stretch at 1700 cm^{-1} and the Si−O stretch is observed between 1100 and 1000 cm^{-1}. The Si−CH$_3$ and Si−CH groups, in the methyl- and isopropyl-substituted polymers, absorb at approximately 1250 and 1200 cm^{-1}, and the Si−C (aromatic) group displays bands at 1430 and 1110 cm^{-1}. The expected absorbances for the aromatic ($>$3000 cm^{-1}) and aliphatic ($<$3000 cm^{-1}) C−H stretches are also present in the spectra of the various polymers.

Thermal analysis by DSC provided determination of the glass transition temperatures (T_g) of these poly(silyl ester)s (Table 1). Each of the polymers was a transparent viscous fluid or a slightly waxy solid with T_g's well below room temperature, and the relative values of the T_g's correlated with the differences in the polymer compositions. For example, the isopropyl groups attached to the silicon in **1b** increase the free volume of the polymer chain and therefore lower the glass transition temperature, in comparison to the case for the methyl-substituted **1a**, and the phenyl groups in **1c** increase the T_g by decreasing the flexibility of the polymer. These same effects can be observed in polymers **3a**−**c**. Comparison of the T_g's for **1a**−**c** with those of **3a**−**c** indicates that changing the silyl ester monomer from bis(trimethylsilyl) adipate, a six-carbon chain, to bis(trimethylsilyl) sebacate, a ten-carbon chain, has little to no effect on the glass transition temperature of the isopropyl- and phenyl-substituted polymers; however, there is a lower glass transition temperature found for the methyl-substituted polymer, **3a,** than for **1a**. However, it should be noted that the degrees of polymerization of these polymers are low and could have a lowering effect on the measured T_g's due to end-group effects. Polymers **2a**−**c**, which all have methyl groups attached as side groups to the silicon atoms, have less variation in their T_g's than observed within the other two series. The glass transition temperatures of these methyl-substituted silicon adipate-based polymers, **2a**−**c**, are similar to that of **1a**, which would be expected, since it also has methyl substituents on the silicon atoms and an adipate comonomer unit.

The thermal stabilities of the poly(silyl ester)s were evaluated for polymers **2a**−**c** by TGA from 30 to 500 °C. Once again, due to the low degrees of polymerization of the polymers, the TGA data is affected by the higher concentration of end groups. Polymer **2a** was found to be the most thermally labile, beginning to decompose at around 100 °C and experiencing nearly 100% mass loss by 370 °C. This is in contrast to **2b**, which did not begin to lose mass until 190 °C and lost about 90% of its mass by 470 °C. Although both **2a** and **2b** have similar compositions, the molecular weight of **2a** is much less than that of **2b**, which can affect the thermal analysis and indicates the presence of more small molecules in **2a** that could lead to a lower temperature for onset of mass loss. Polymer **2c**, which contains aromatic rings in the backbone, was found to be much more stable toward thermal degradation than either **2a** or **2b**, and there are two distinct mass loss steps in the TGA of **2c**. In the first step, 47% mass loss occurs between 230 and 410 °C. The polymer continues to lose mass in a discrete second step from 410 °C, but 25% of the original weight remains at 500 °C.

Many factors can affect the stability of poly(silyl ester)s toward nucleophilic degradation, including the steric and electronic effects of the substituents on the silicon atoms and the composition and physical properties (i.e. hydrophobicity, solubility, and crystallinity) of the polymer backbone. The silicon substituents control the local electrophilic character for the silicon as well as its accessibility. Since nucleophilic attack can occur either at the silicon or at the carbonyl carbon, changing the steric hindrance and altering the electronic environment around the silicon changes the amount and rate of polymer degradation, by altering the rate and mechanism of silyl ester cleavage.[20,21] Hydrolysis and alcoholysis experiments were performed on solutions of the polymers in tetrahydrofuran (THF), to probe effects relating to the chemical properties, while minimizing dependence upon physical properties.

The extent of hydrolysis and alcoholysis was evaluated by GPC analyses of molecular-weight loss with time for the polymers in THF solutions of 5% water, 1%

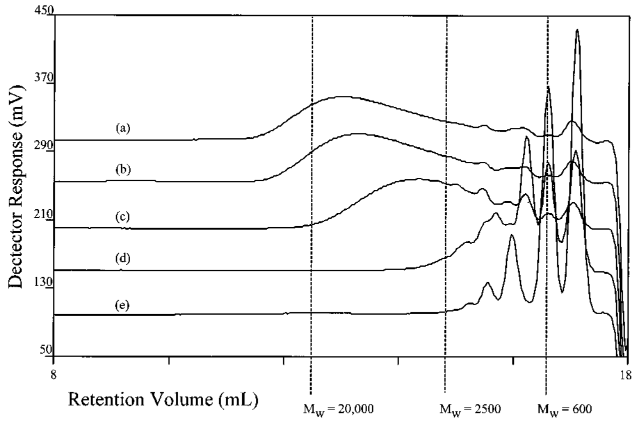


Figure 1. Gel permeation chromatograms of polymer **2b** as a solution in THF containing 1% *tert*-butanol after (a) 5 min, (b) 1 h, (c) 4 h, (d) 8 h, and (e) 72 h.

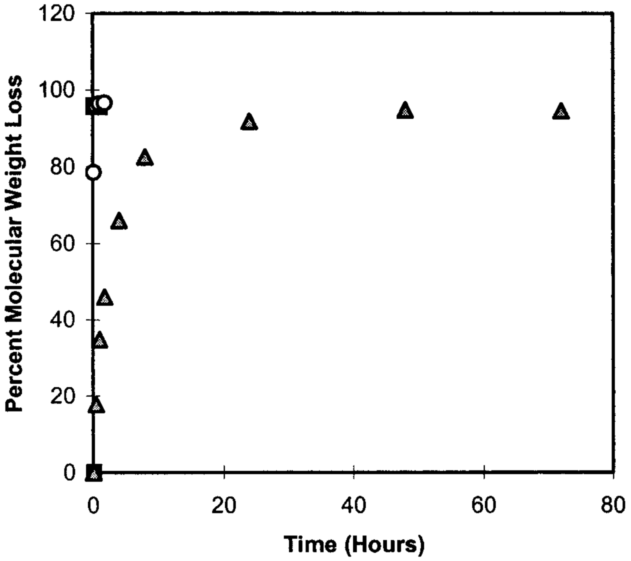


Figure 2. Plot of percentage of molecular weight lost vs time for comparison of the relative rates of degradation of **2b** in (■) 5% H_2O/THF, (○) 1% MeOH/THF, and (▲) 1% *tert*-BuOH/THF.

methanol, and 1% *tert*-butanol (volume/volume) in accordance with degradation studies of poly(silyl ester)s published previously. The hydrolysis of polymer **2b** was noted in THF solutions with both 1% water and 5% water added, to confirm that the relative water concentration in THF did not affect the polymer degradation behavior. In all cases, an excess of water or alcohol was used. Figure 1 shows the SEC chromatograms of a typical degradation experiment; the decreasing molecular weight of **2b** in a 1% *tert*-butanol/THF solution over time is observed. Each of the polymers exhibited a greater stability toward the *t*-BuOH than the MeOH than the H_2O, which can be seen in Figure 2, showing the degradation of **2b**. The degradation data for poly(silyl ester)s **2a**, **2b**, and **2c** are given in Table 2. As previously reported for polymers **1a**−**c**, the substituents attached to the silicon atoms greatly affect the relative degradation rates for the polymers. The sterically bulky isopropyl-substituted polymer, **1b**, was found to be substantially more stable than the methyl- and phenyl-substituted polymers, **1a** and **1c**, which had similar degradation rates in all three solutions. Both steric and electronic factors contribute to the observed degradation rates by either slowing the rate of nucleophilic attack at the silicon or altering the mechanism of nucleophilic attack and cleavage. The same effect was noted for polymers **3a**−**c** (Table 3), whose degradation rates are similar to those previously reported for **1a**−**c**: changing the chain length of the repeat unit does not appear to affect the polymer stabilities. Polymers **1a**−**c** and **3a**−**c** are based upon disiloxane monomers (**6a**−**c**), where the silicon atoms are connected by an electronegative oxygen atom, causing an increase in the electrophilicity of the silicon and thereby making it more susceptible toward nucleophilic attack, in comparison to trialkyl-substituted silyl esters. This is demonstrated with **2a**−**c**, in which the aliphatic and aliphatic−aromatic chains bridging the silicon atoms in polymers **2a**−**c** result in polymers that exhibit higher stabilities than those for **1a** and **3a**, the corresponding siloxane-based poly(silyl ester)s (Table 3 and Figure 3). However, the isopropyl-substituted polymers (**1b** and **3b**) remain the most stable of the materials.

Preliminary studies of the degradation of poly(silyl ester)s in the solid state were also performed on polymer **2a** so as to compare the rate and mechanism of degradation in the solution state to those in the solid state. Samples of **2a**, which is a transparent viscous fluid, were transferred via pipet into glass vials and exposed to the environment in the laboratory, at approximately 70 °C and 40% humidity, where nucleophilic degradation can occur through the attack by atmospheric water. The polymer degradation was observed by SEC and ^{29}Si NMR (Figures 4 and 5). The SEC traces showed unusual behavior, with the growth of a peak at long retention time due to cleavage of the polymer, while polymeric material remained. Calculations indicated that the number average molecular weight (M_n) decreased, but the overall M_w of the polymer was unchanged, or increased slightly. Therefore, ^{29}Si NMR was employed to more accurately monitor hydrolysis of the silyl ester bonds. The change in chemical shift of the silicon atoms from 23 ppm for the silyl ester to 8 ppm for the silanol or its silyl ether condensation products[34] was noted over time (Figure 5). These observations can be explained by the hydrolysis of the silyl ester linkages by reaction with atmospheric water, to give silanols as degradation products. In the solid state, these silanols then easily condense to form a poly(ene-siloxane), which could account for the polymer noted in the SEC, since the ^{29}Si NMR no longer contained a resonance for silyl esters. Further investigation into this unusual phenomenon is underway.

Conclusion

Variability in the degradation behavior of poly(silyl ester)s has been demonstrated. The polymers degrade rapidly in the presence of nucleophilic agents. Experiments to determine the mechanism of hydrolysis and alcoholysis of these polymers including the extent of nucleophilic attack at the silicon versus the carbonyl carbon are in progress. Further degradation studies of the polymers in the solid state are also being done to analyze the ability of the poly(silyl ester)s to serve as solid, degradable materials in applications such as matrices for drug release, temporary coatings, temporary adhesives, or other purposes.

Experimental Section

General Directions. All manipulations of reagents and reactions were performed under argon on a double manifold,

Table 2. Molecular Weight Data (M_w from GPC) for the Degradation Studies of Poly(silyl ester)s 2a–c as Solutions in (a) 5% Water/THF, (b), 1% Water/THF, (c), 1% Methanol/THF, (d) or 1% *tert*-Butanol/THF

	2a			2b				2c		
time	a	c	d	a	b	c	d	a	c	d
0	3360	3360	3360	9760	6210	9760	9760	8560	8560	8560
5 min	200	2440	3200	410	690	2090	9760	480	530	8560
30 min	150	1460	3220	420	680	410	8020	460	500	6820
1 h		990	3280	420		350	6960	440	480	5030
2 h		530	3210			330	5270		500	3390
4 h		230	3030				3320			2160
8 h			2280				1700			1460
24 h			1240				790			900
48 h			500				510			540
72 h							530			560

Table 3. Molecular Weight Data (M_w from GPC) for the Degradation Studies of Poly(silyl ester)s 3a–c as Solutions in (a) 5% Water/THF, (b), 1% Methanol/THF, (c) or 1% *tert*-Butanol/THF

	3a			3b			3c		
time	a	b	c	a	b	c	a	b	c
0	2400	2400	2400	3220	3220	3220	2050	2050	2050
5 m	90	1230	1550	2990	3170	3000	310	1730	1880
30 m	100	1160	1660	2500	3090	2940	380	960	1280
1 h		940	1570	1650	2920	2920		780	1070
2 h		700	1610	1330	2890	2910		690	890
4 h		610	1170	850	2860	2770		640	720
8 h		480	920					520	560
24 h			510		2620			240	380
32 h		280				2520			
48 h		210	670						
96 h		200							
120 h			320		590	1290			
167 h			340		360	1470			

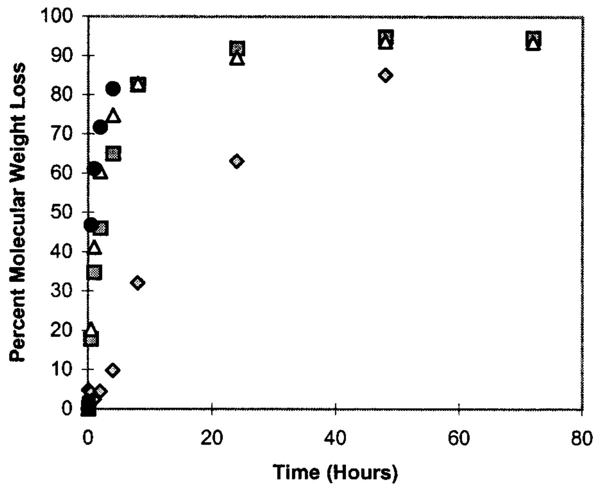


Figure 3. Plot of percentage of molecular weight lost *vs.* time for comparison of the relative rates of degradation of (●) **1a**, (◆) **2a**, (■) **2b**, and (△) **2c** in 1% *tert*-BuOH/THF.

and all glassware was flame-dried under vacuum. ^{1}H NMR spectra were recorded on a Varian Unity-plus (300 MHz) spectrometer with the solvent proton signal as standard. ^{13}C NMR spectra were recorded at 75 MHz on a Varian Unity-plus spectrometer with the solvent carbon signal as standard. ^{29}Si NMR spectra were recorded using standard INEPT[35] (Insensitive Nuclei Enhanced by Polarization Transfer) experiments on a Varian Unity-plus spectrometer at 59.6 MHz and were referenced externally to tetramethylsilane at 0 ppm. IR spectra were obtained on a Mattson polaris spectrometer as thin films on NaCl disks. Size exclusion chromatography was conducted with a Hewlett-Packard series 1050 HPLC, and detection was by a Hewlett-Packard 1047A refractive index detector and a Viscotek model 110 differential viscometer; data analysis was performed with Trisec GPC Software, versions 2.70 and 3.00 (Viscotek Corp.). Two 5-μm Polymer Laboratories PLgel columns (300 mm × 7.7 mm) connected in series in order of increasing pore size (500 Å, mixed bed D) were used with THF distilled from sodium or calcium hydride as the eluent. Molecular weights were based on polystyrene standards (Polymer Laboratories Ltd.). Glass transition temperatures were measured by differential scanning calorimetry on a Perkin-Elmer DSC 4 differential scanning calorimeter. Heating rates were 10 °C/min. T_g was taken as the midpoint of the inflection tangent. Thermogravimetric analyses were done on a Perkin-Elmer TGS-2 thermogravimetric analyzer. For both DSC and TGA, the Perkin-Elmer instruments were upgraded with an Instrument Specialists, Inc. (Antioch, IL) temperature program interface-PE, and data were acquired and analyzed using TA-PC software version v. 2.11a (Instrument Specialists Inc.). Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN) or MHW Laboratories (Phoenix, AZ) and are reported for unpurified polymers.

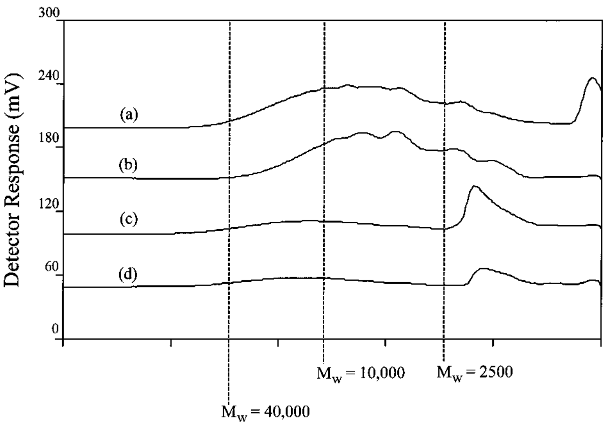


Figure 4. Gel permeation chromatograms monitoring the degradation of polymer **2a** in air at *ca.* 70 °C and 40% humidity after (a) 5 min, (b) 1 h, (c) 4 h, and (d) 24 h.

Materials. 1,3-Dichlorotetramethyldisiloxane, 1,3-dichlorotetraisopropyldisiloxane, 1,3-dichlorotetraphenyldisiloxane, 1,2-bis(chlorodimethylsilyl)ethane, 1,6-bis(chlorodimethylsilyl)hexane, and bis((chlorodimethylsilyl)ethyl)benzene were purchased from United Chemical Technologies and distilled prior

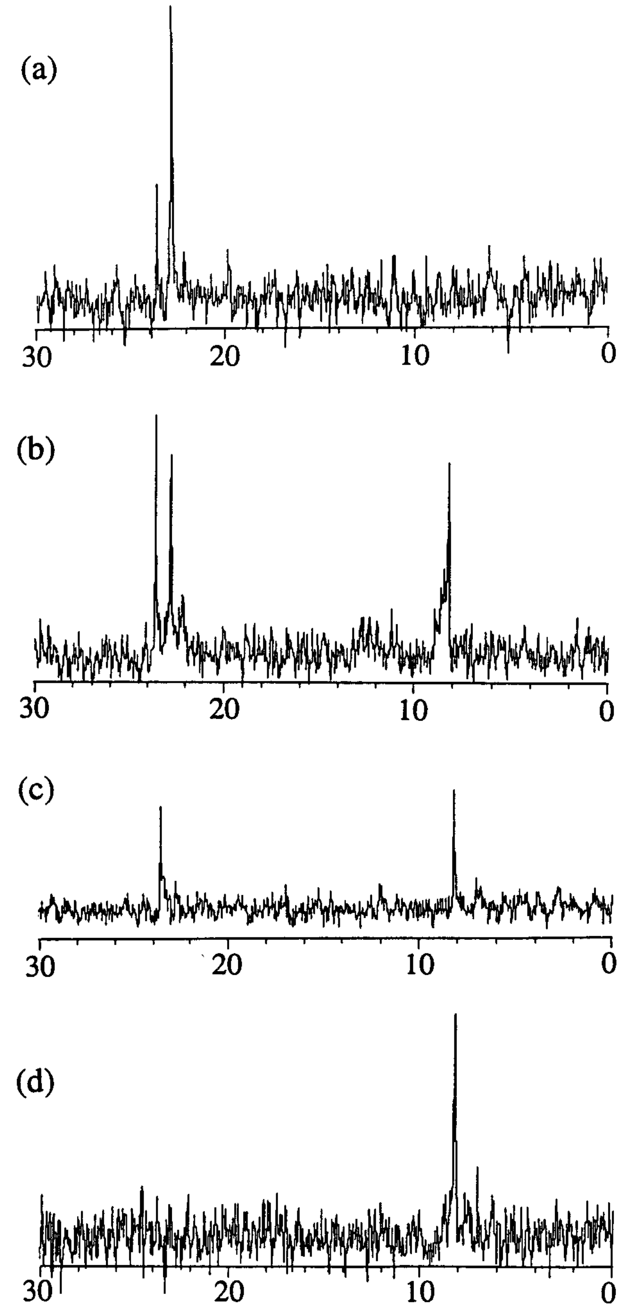


Figure 5. ^{29}Si NMR (THF-d_8) spectra monitoring the degradation of polymer **2a** in air after (a) 5 min, (b) 30 min, (c) 2 h, and (d) 24 h.

to use. Adipic acid, sebacic acid, and 1,1,1,3,3,3-hexamethyldisilazane (HMDS) were obtained from Aldrich Co. and used as received. *N*,*N*-Dimethylformamide (DMF) was purchased from Aldrich Co. and distilled under reduced pressure from CaO. Tetrahydrofuran (THF) omnisolv grade was purchased from EM Science and distilled from sodium/benzophenone. Methanol and *tert*-butanol were obtained from Fisher Scientific and distilled from sodium.

General Procedure for the Synthesis of Poly(silyl ester)s. The appropriate bis(trimethylsilyl) ester was distilled into a tared 10-mL round-bottom flask or reaction tube. To the flask containing the silyl ester was added via syringe 1 equiv of the appropriate silyl chloride (freshly distilled under argon). Dimethylformamide was added via syringe for the preparation of **2a**−**c**. The reaction was typically allowed to stir under argon at 100 °C for 1−2 weeks. During the polymerization the TMSCl was removed by evaporation. Due to the hydrolytic sensitivities of the polymers, no further purification techniques were performed.

Poly(tetramethyldisilyloxyl adipate) (1a). This was prepared from the reaction of **4** (0.8715 g, 3.004 mmol) with **5a** (0.6519 g, 3.0307 mmol) at 100 °C for 3 days and then at 125 °C for 8 days. $T_g = -56$ °C. IR (NaCl) 2889, 1657, 1127, 989 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.29 (br s, 12H, Si(C$\boldsymbol{H}_3$)$_2$), 1.63 (br m, 4H, COCH$_2$C$\boldsymbol{H}_2$), 2.33 (br m, 4H, COC$\boldsymbol{H}_2$CH$_2$) ppm. ^{13}C NMR (75.4 MHz, CDCl$_3$) δ −0.50 (Si($\boldsymbol{C}$H$_3$)$_2$), 24.16 (COCH$_2\boldsymbol{C}$H$_2$), 35.37 (CO$\boldsymbol{C}$H$_2$CH$_2$), 173.05 (carbonyl) ppm. ^{29}Si NMR INEPT (59.6 MHz, CDCl$_3$) δ −7.48 ppm. $M_w = 2850$; $M_w/M_n = 2.2$. Anal. Calcd for $(C_{10}H_{20}O_5Si_2)_n$ $(276.44)_n$: C, 43.45; H, 7.29. Found: C, 43.30; H, 7.64.

Poly(tetraisopropyldisilyloxyl adipate) (1b). This was prepared from the reaction of **4** (1.1325 g, 3.270 mmol) with **5b** (1.0318 g, 3.2711 mmol) at 135 °C for 14 days. $T_g = -84$ °C. IR (NaCl) 2947, 2875, 1728, 1255, 1064, 1003, 889 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.07 (d, 24H, $J = 6$ Hz, Si(CH(C$\boldsymbol{H}_3$)$_2$)$_2$), 1.19 (septet, 4H, $J = 6$ Hz, Si(C$\boldsymbol{H}$(CH$_3$)$_2$)$_2$), 1.67 (br m, 4H, COCH$_2$C$\boldsymbol{H}_2$), 2.37 (br m, 4H, COC$\boldsymbol{H}_2$CH$_2$) ppm. ^{13}C NMR (75.4 MHz, CDCl$_3$) δ 12.80 (Si($\boldsymbol{C}$H(CH$_3$)$_2$)$_2$), 16.66 (Si(CH($\boldsymbol{C}$H$_3$)$_2$)$_2$), 24.39 (COCH$_2\boldsymbol{C}$H$_2$), 35.34 (CO$\boldsymbol{C}$H$_2$CH$_2$), 172.43 (carbonyl) ppm. ^{29}Si NMR INEPT (59.6 MHz, CDCl$_3$) δ −11.38 ppm. $M_w = 2700$; $M_w/M_n = 1.7$. Anal. Calcd for $(C_{18}H_{36}O_5Si_2)_n$ $(388.65)_n$: C, 55.63; H, 9.34. Found: C, 52.86; H, 9.40.

Poly(tetraphenyldisilyloxyl adipate) (1c). This was prepared from the reaction of **4** (0.5996 g, 2.064 mmol) with **5c** (0.9226 g, 2.043 mmol) at 115 °C for 3 days followed by 4 days at 125 °C and then 3 days at 135 °C. $T_g = 2.7$ °C. IR (NaCl) 2947, 2875, 1728, 1590, 1465, 1255, 1188, 1064, 1003, 889, 761 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.41 (br m, 4H, COCH$_2$C$\boldsymbol{H}_2$), 2.18 (br m, 4H, COC$\boldsymbol{H}_2$CH$_2$), 7.35 (m, 12H, aromatic), 7.68 (m, 8H, aromatic) ppm. ^{13}C NMR (75.4 MHz, CDCl$_3$) δ 23.91 (COCH$_2\boldsymbol{C}$H$_2$), 35.19 (CO$\boldsymbol{C}$H$_2$CH$_2$), 127.80 (aromatic), 130.78 (aromatic), 131.70 (aromatic), 134.23 (aromatic), 172.30 (carbonyl) ppm. ^{29}Si NMR INEPT (59.6 MHz, CDCl$_3$) δ −36.99 ppm. $M_w = 2650$; $M_w/M_n = 1.9$. Anal. Calcd for $(C_{30}H_{28}O_5Si_2)_n$ $(524.72)_n$: C, 68.67; H, 5.38. Found: C, 66.46; H, 5.14.

Poly[bis(dimethylsilyl)ethyl adipate] (2a). This was prepared from the reaction of **4** (1.6557 g, 5.6993 mmol) with **6a** (1.2207 g, 5.6706 mmol) and the addition of DMF (0.05 mL, 0.65 mmol, 12%). The polymerization was allowed to proceed with stirring under an argon atmosphere at 100 °C for 14 days. $T_g = -56$ °C. IR (NaCl) 2980−2880, 1740−1690, 1470, 1420, 1370−1180 (br), 1060, 970, 940−760 (br) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.20 [12H, s, (Si(C$\boldsymbol{H}_3$)$_2$CH$_2$)$_2$], 0.62 [4H, s, (Si(CH$_3$)$_2$C$\boldsymbol{H}_2$)$_2$], 1.56 [4H, br s, (CO$_2$CH$_2$C$\boldsymbol{H}_2$)$_2$], 2.26 [4H, br s, (CO$_2$C$\boldsymbol{H}_2$CH$_2$)$_2$] ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ −2.63 [(Si($\boldsymbol{C}$H$_3$)$_2$CH$_2$)$_2$], 6.93 [(Si(CH$_3$)$_2\boldsymbol{C}$H$_2$)$_2$], 24.24 [(CO$_2$CH$_2\boldsymbol{C}$H$_2$)$_2$], 35.32 [(CO$_2\boldsymbol{C}$H$_2$CH$_2$)$_2$], 173.76 (carbonyl) ppm. ^{29}Si NMR INEPT (59.6 MHz, CDCl$_3$) δ 23.84 ppm. $M_w = 3360$; $M_w/M_n = 2.1$. Anal. Calcd for $(C_{12}H_{24}O_4Si_2)_n$ $(288.49)_n$: C, 49.96; H, 8.39. Found: C, 49.01; H, 8.60.

Poly[bis(dimethylsilyl)hexyl adipate] (2b). This was prepared from the reaction of **4** (1.3668 g, 4.7048 mmol) with **6b** (1.2740 g, 4.6945 mmol) and the addition of DMF (0.05 mL, 0.65 mmol, 14%), heated at 100 °C for 14 days. $T_g = -62$ °C. IR (NaCl) 2955−2856, 1717, 1455, 1413, 1369, 1254, 1186, 1148, 1059, 922, 847−795 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.23 (s, 12H, Si(C$\boldsymbol{H}_3$)$_2$), 0.71 [br m 4H, (Si(CH$_3$)$_2$C$\boldsymbol{H}_2$CH$_2$CH$_2$)$_2$], 1.29 [br m, 8H, (Si(CH$_3$)$_2$CH$_2$C$\boldsymbol{H}_2$C$\boldsymbol{H}_2$)$_2$], 1.60 [br m, 4H, (COCH$_2$C$\boldsymbol{H}_2$)$_2$], 2.29 [br m, 4H, (COC$\boldsymbol{H}_2$CH$_2$)$_2$] ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ −1.83 (Si($\boldsymbol{C}$H$_3$)$_2$), 15.96 [(Si(CH$_3$)$_2\boldsymbol{C}$H$_2$CH$_2$CH$_2$)$_2$], 22.70 [(Si(CH$_3$)$_2$CH$_2\boldsymbol{C}$H$_2$CH$_2$)$_2$], 24.37 [(Si(CH$_3$)$_2$CH$_2$CH$_2\boldsymbol{C}$H$_2$)$_2$], 32.79 [(COCH$_2\boldsymbol{C}$H$_2$)$_2$], 35.49 [(CO$\boldsymbol{C}$H$_2$CH$_2$)$_2$], 173.88 (carbonyl) ppm. ^{29}Si NMR INEPT (59.6 MHz, CDCl$_3$) δ 23.48 ppm. $M_w = 9760$; $M_w/M_n = 3.9$. Anal. Calcd for $(C_{16}H_{32}O_4Si_2)_n$ $(344.60)_n$: C, 55.77; H, 9.36. Found: C, 54.86; H, 8.60.

Poly[bis((dimethylsilyl)ethyl)benzyl adipate] (2c). This was prepared from the reaction of **4** (1.0213 g, 3.5155 mmol) with **6c** (1.1303 g, 3.5386 mmol) and the addition of DMF (0.02 mL, 0.2583 mmol, 7.3%), heated at 100 °C for 14 days. $T_g = -37$ °C. IR (NaCl) 3030−3019, 2957−2874, 1716, 1600−1575, 1455, 1410, 1370, 1315, 1253, 1181, 1148, 1059, 1010, 919, 850−795 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.15 (s, 12H, 23% of isomer, ($Si(C\boldsymbol{H}_3)_2CHCH_3)_2C_6H_4$), 0.26 (s, 12H, 77% of isomer, ($Si(C\boldsymbol{H}_3)_2CH_2CH_2)_2C_6H_4$), 1.11 (br t, 4H, 77% of isomer, ($Si(CH_3)_2C\boldsymbol{H}_2CH_2)_2C_6H_4$), 1.34 (br d, 6H, 23% of isomer, ($Si(CH_3)_2CHC\boldsymbol{H}_3)_2C_6H_4$), 1.62 (br m, 4H, ($CO_2CH_2C\boldsymbol{H}_2)_2$), 2.31 (br t, 4H, ($CO_2C\boldsymbol{H}_2CH_2)_2$), 2.51 (br q, 2H, 23% of isomer, ($Si(CH_3)_2C\boldsymbol{H}CH_3)_2C_6H_4$), 2.65 (br t, 4H, 77% of isomer, ($Si(CH_3)_2CH_2C\boldsymbol{H}_2)_2C_6H_4$), 7.00−7.18 (br m, 4H, aromatic) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.79 [($Si(\boldsymbol{C}H_3)_2CH_2CH_2)_2C_6H_4$], 14.12 [($Si(CH_3)_2CH\boldsymbol{C}H_3)_2C_6H_4$], 17.92 [($Si(CH_3)_2\boldsymbol{C}H_2CH_2)_2C_6H_4$], 21 [($Si(CH_3)_2\boldsymbol{C}HCH_3)_2C_6H_4$, too small to observe], 24.39 [($CO_2CH_2\boldsymbol{C}H_2)_2$], 28.88 [($Si(CH_3)_2CH_2\boldsymbol{C}H_2)_2C_6H_4$], 35.45 [($CO_2\boldsymbol{C}H_2CH_2)_2$], 124.49 (aromatic), 125.18 (aromatic), 127.29 (aromatic), 127.73 (aromatic), 128.31 (aromatic), 143.99 (aromatic), 173.83 (carbonyl) ppm. ^{29}Si NMR INEPT (59.6 MHz, $CDCl_3$) δ 23.09, 20.69 ppm. $M_w = 8560$; $M_w/M_n = 3.4$. Anal. Calcd for $(C_{20}H_{24}O_4Si_2)_n$ $(384.58)_n$: C, 62.46; H, 6.29. Found: C, 59.75; H, 8.14.

Poly(tetramethyldisilyloxyl sebacate) (3a). This was prepared from the reaction of **7** (1.3371 g, 3.8608 mmol) with **5a** (0.7894 g, 3.8845 mmol), heated at 100 °C for 14 days. $T_g = -77$ °C. IR (NaCl) 2961, 2855, 1731, 990 cm^{-1}. ^1H NMR (300 MHz $CDCl_3$) δ 0.11 (s, 12H, $Si(C\boldsymbol{H}_3)_2$), 1.33 (m, 8H, $COCH_2CH_2C\boldsymbol{H}_2C\boldsymbol{H}_2$), 1.63 (m, 4H, $COCH_2C\boldsymbol{H}_2CH_2CH_2$), 2.34 (br t, 4H, $J = 7$ Hz, $COC\boldsymbol{H}_2CH_2CH_2CH_2$) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$) δ −0.26 ($Si(\boldsymbol{C}H_3)_2$), 24.85 ($COCH_2\boldsymbol{C}H_2CH_2CH_2$), 29.03 ($COCH_2CH_2\boldsymbol{C}H_2CH_2$), 29.90 ($COCH_2CH_2CH_2\boldsymbol{C}H_2$), 35.85 ($CO\boldsymbol{C}H_2CH_2CH_2CH_2$), 174.00 (carbonyl) ppm. ^{29}Si NMR INEPT (59.6 MHz, $CDCl_3$) δ −7.46 ppm. $M_w = 2400$ g/mol; $M_w/M_n = 2.3$. Anal. Calcd for $(C_{14}H_{28}O_5Si_2)_n$ $(332.54)_n$: C, 50.57; H, 8.49. Found: C, 48.67; H, 8.92.

Poly(tetraisopropyldisilyloxyl sebacate) (3b). This was prepared from the reaction of **7** (1.7756 g, 6.1206 mmol) with **5b** (1.9307 g, 6.1208 mmol), heated at 110 °C for 2 days and then at 165 °C for 13 days. $T_g = -85$ °C. IR (NaCl) 3031, 2980, 1657, 1225, 1075, 871 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 1.05 (d, 24H, $J = 6$ Hz, $Si(CH(C\boldsymbol{H}_3)_2)_2$), 1.18 (septet, 4H, $J = 6$ Hz, $Si(C\boldsymbol{H}(CH_3)_2)_2$), 1.26 (br m, 8H, $COCH_2CH_2C\boldsymbol{H}_2C\boldsymbol{H}_2$), 1.60 (br m, 4H, $COCH_2C\boldsymbol{H}_2CH_2CH_2$), 2.25 (br t, 4H, $J = 8$ Hz, $COC\boldsymbol{H}_2CH_2CH_2CH_2$) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 12.85 ($Si(\boldsymbol{C}H(CH_3)_2)_2$), 16.71 ($Si(CH(\boldsymbol{C}H_3)_2)_2$), 25.01 ($COCH_2\boldsymbol{C}H_2CH_2CH_2$), 29.12 ($COCH_2CH_2\boldsymbol{C}H_2CH_2$), 29.20 ($COCH_2CH_2CH_2\boldsymbol{C}H_2$), 35.79 ($CO\boldsymbol{C}H_2CH_2CH_2CH_2$), 172.50 (carbonyl) ppm. ^{29}Si NMR INEPT (59.6 MHz, $CDCl_3$) δ −11.35 ppm. $M_w = 3220$; $M_w/M_n = 1.9$. Anal. Calcd for $(C_{22}H_{44}O_5Si_2)_n$ $(44.76)_n$: C, 59.41; H, 9.97. Found: C, 56.07; H, 9.56.

Poly(tetraphenyldisilyloxyl sebacate) (3c). This was prepared from the reaction of **7** (1.5107 g, 4.3622 mmol) with **5c** (1.9659 g, 4.3542 mmol), heated at 110 °C for 7 days and then at 125 °C for 4 days. $T_g = -6.4$ °C. IR (NaCl) 3081, 2932, 2865, 1738, 1589, 1435, 1249, 1177, 1126, 1090, 936, 704 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 1.20 (br m, 8H, $COCH_2CH_2C\boldsymbol{H}_2C\boldsymbol{H}_2$), 1.50 (br m, 4H, $COCH_2C\boldsymbol{H}_2CH_2CH_2$), 2.26 (br t, 4H, $J = 7$ Hz, $COC\boldsymbol{H}_2CH_2CH_2CH_2$), 7.30−7.55 (m, 12H, aromatic), 7.71 (d, 8H, $J = 1$ Hz, aromatic) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 24.66 ($COCH_2\boldsymbol{C}H_2CH_2CH_2$), 28.93 ($COCH_2CH_2\boldsymbol{C}H_2CH_2$), 29.09 ($COCH_2CH_2CH_2\boldsymbol{C}H_2$), 35.65 ($CO\boldsymbol{C}H_2CH_2CH_2CH_2$), 127.76 (aromatic), 130.72 (aromatic), 131.67 (ipso aromatic), 134.79 (aromatic), 173.00 (carbonyl) ppm. ^{29}Si NMR INEPT (59.6 MHz, $CDCl_3$) δ −37.09 ppm. $M_w = 2040$ g/mol; $M_w/M_n = 1.8$. Anal. Calcd for $(C_{34}H_{36}O_5Si_2)_n$ $(580.83)_n$: C, 70.31; H, 6.25. Found: C, 67.09; H, 5.87.

Degradation of Polymers in Solution. Approximately 20 mg of polymer was dissolved in 2 mL of tetrahydrofuran. Water (0.10 mL, 5%), methanol (0.02 mL, 1%), or *tert*-butanol (0.02 mL, 1%) was added to the solution of polymer. At 5 min, 30 min, 1 h, 2 h, 4 h, 8 h, 24 h, and 48 h, 0.1 mL of the polymer solution was injected into the GPC and the resulting chromatogram was analyzed.

Degradation of Polymer 2a in Air. Eight samples of approximately 10 mg each of the polymer were placed in individual glass vials. The vials were open to the environment, which was 68−70 °C with 40−42% humidity. At the appropriate times (5 min, 30 min, 1 h, 2 h, 4 h, 8 h, 24 h, and 48 h), the polymer samples were dissolved in THF-d_8 and the ^1H NMR spectrum, the ^{29}Si NMR spectrum, and the gel permeation chromatogram were obtained.

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