Synthesis, Characterization and Degradation of Poly(silyl ester)s

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ABSTRACT: To investigate the effects of sterics and polymer backbone composition upon the rates of hydrolytic degradation of polymers containing trialkyl-substituted silyl ester linkages, six poly(silyl ester)s with molecular weights typically ranging from 5000 to 15000 Da were synthesized through transsilylation ester exchange reactions of alkyl or aryl bis(trimethylsilyl)esters with methyl- and isopropyl-substituted bis(chlorosilyl)hexanes to give trimethylsilyl chloride as the condensate. Characterization of the poly(silyl ester)s included infrared spectroscopy (IR), ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR INEPT spectroscopies, size-exclusion chromatography (SEC), differential scanning calorimetry, and thermogravimetric analysis. Both ^{29}Si NMR and SEC were employed to monitor the polymerization and the degradation experiments. As expected, the relative stability of the silyl ester bonds toward hydrolysis increased with increased steric hindrance of the substituents attached to the silicon atoms. The incorporation of *p*-phenylene groups into the polymer backbone allowed for the formation of crystalline domains, which in turn greatly increased the stability toward hydrolytic degradation of the polymers in the solid state. Hydrolysis of the polymers containing diisopropyl-substituted silyl esters gave small molecules; however, degradation of the dimethyl-substituted poly(silyl ester)s as solids in air resulted in the formation of poly(dimethylsilylhexylene siloxane) from the spontaneous condensation of 1,6-bis(dimethylhydroxysilyl)hexane.

Introduction

Polymers with high strength and excellent mechanical properties during long-time service are most often considered as technological materials; however, degradable polymers are playing an increasingly important role as commodity materials that account for environmental concerns[1,2] and also as materials for applications in biomedicine.[3] Studies involving hydrolytically degradable materials have focused mainly upon poly(ester)s,[4−9] because of the presence of labile ester functional groups along the polymer backbone and the breakdown into naturally occurring hydroxy acids. The use of alternative hydrolytically labile functionalities have produced poly(anhydride)s,[10−15] poly(ortho ester)s,[16−18] poly(organophosphazene)s,[19−21] and poly(silazane)s.[22] Poly(anhydride)s have demonstrated more rapid degradation than poly(ester)s, leading to a surface-erosion degradation mechanism, which has been shown to be important for controlled release applications.[14,15] Even with the large number of degradable polymers available, control and variability over the amount and rate of degradation remain somewhat limited to longer degradation times without the addition or incorporation of catalytic (e.g., acidic) excipients.[16]

The development of a polymer material based upon a functionality that provides broadly attunable rates of hydrolysis resulting from slight variations in polymer composition is expected to be quite useful as a single-component homopolymeric degradable material. Poly(silyl ester)s were recently reported as a new class of degradable polymers, in which the highly labile silyl ester linkage allowed for rapid degradation of the polymer materials.[23,24] The relative rates of degradation for the poly(silyl ester)s follow the trends for small molecule silyl esters, which are often used as protecting groups for carboxylic acids:[25−27] increased steric hindrance and decreased electrophilicity for the silicon substituents lead to longer times required for hydrolytic cleavage. Each of the poly(silyl ester)s was completely cleaved to small molecules within 24 h in the presence of water. Although a variety of poly(silyl ester)s with a range of stabilities have been reported,[23,24] further modifications to the polymer are essential for the production of a single type of degradable system that can demonstrate rates of water degradation ranging from seconds to months.

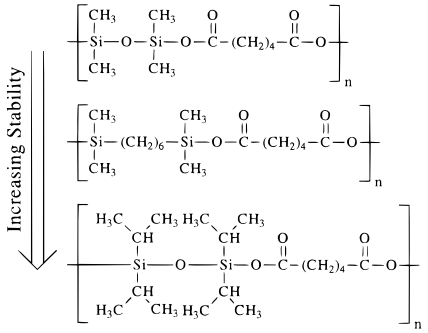

Figure 1. Order of hydrolytic stability for poly(silyl ester)s with variation in the steric and electronic properties of the silicon substituents.

It was shown that silyl ester linkages with dimethylhexyl-substituted silicons gave slower rates of hydrolysis than did dimethyloxy-substituted silyl ester groups. Therefore, replacement of an electronegative oxygen with an alkyl chain decreased the silicon electrophilicity, which in turn decreased the susceptibility toward nucleophilic attack by water. Perhaps surprising was the finding that steric effects dominated the electronic effects, and polymers containing diisopropyloxy-substituted silyl ester groups required the longest time for hydrolytic degradation (Figure 1).[24]

To further attune the degradation properties of this new family of degradable polymers, and to extend the hydrolytic stabilities, we now report the synthesis, characterization, and degradation of polymers on the

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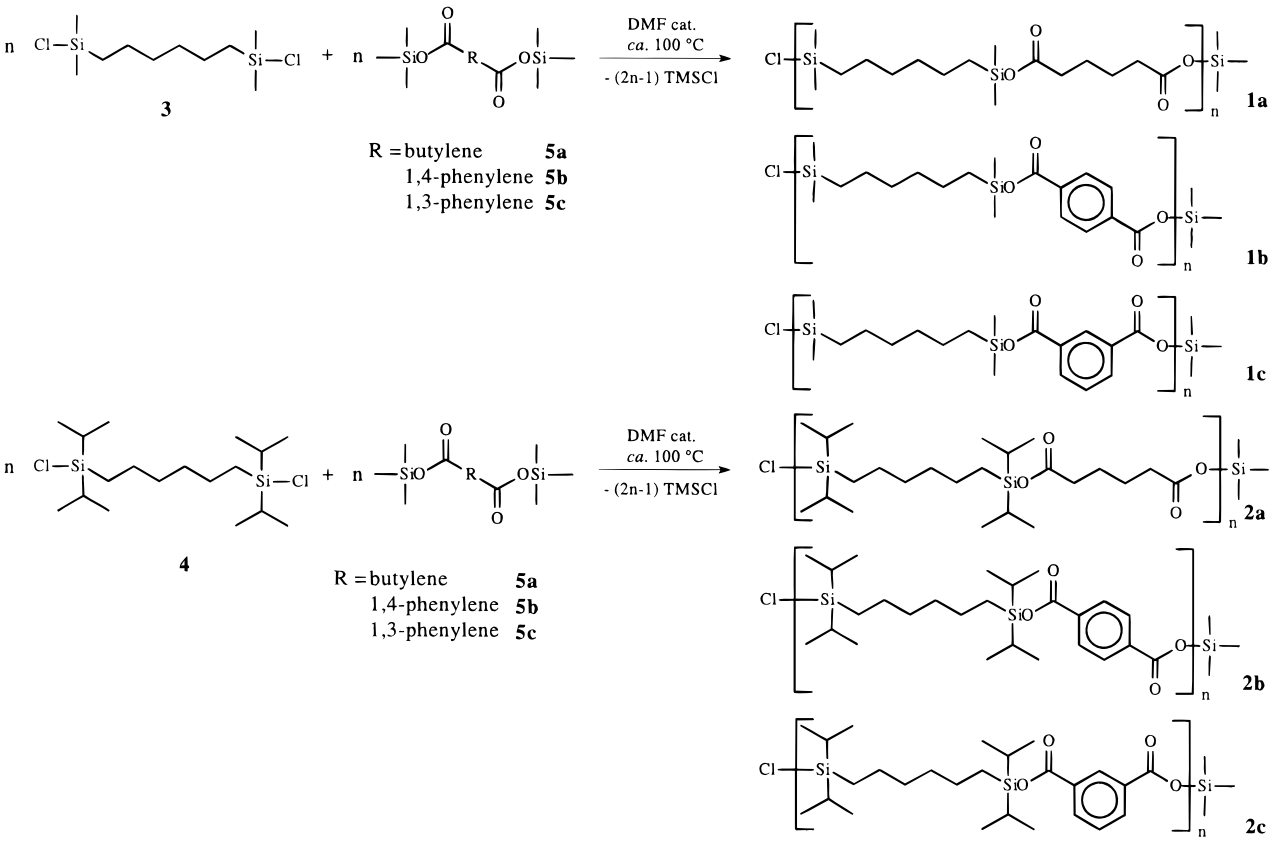
Scheme 1



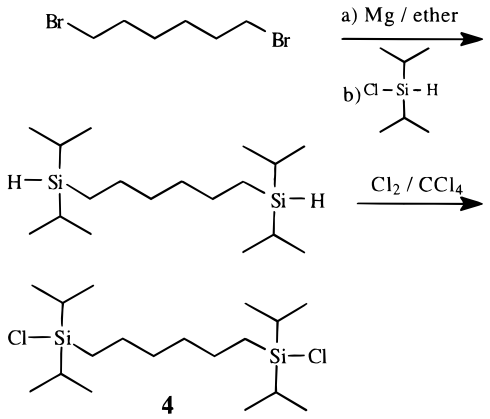
basis of trialkyl-substituted silyl ester linkages with varying side group steric effects. Comparisons of the compositional effects on degradation are made between methyl and isopropyl silicon side chain substituents. Additionally, the effects of variation in the backbone composition, between aliphatic and aromatic backbone linkages adjacent to the carbonyl moieties, upon the physical properties of the polymers and their degradation behavior are investigated.

Results and Discussions

The six poly(silyl ester)s of this study are divided into two series **1a**−**c** and **2a**−**c** (Scheme 1), on the basis of methyl and isopropyl side chain substituents attached to the silicon atoms, respectively. Within each series, the backbone segment between the carbonyl groups differs as *n*-butylene, *p*-phenylene, and *m*-phenylene for **a**, **b**, and **c**, respectively, whereas the backbone segment separating the silicon atoms is held constant as an *n*-hexylene chain. This selection of poly(silyl ester)s provides for the evaluation of the steric effects of trialkyl-substituted silicon atoms forming the silyl ester bonds as well as determination of the effect of chain rigidity and crystallinity upon the hydrolytic stability of the polymer materials.

As was previously reported,[23] the traditional methods for the synthesis of small molecule silyl esters proved to be ineffective for polymer formation. Therefore, the poly(silyl ester)s were prepared by transsilylation ester exchange condensations of the bis(chlorosilyl)hexanes **3** and **4** with the bis(trimethylsilyl)esters **5a**−**c**. All of the polymerizations were performed with freshly distilled monomers at approximately 100 °C under an argon atmosphere for 10−20 days, with the addition of 5−10 molar percent of *N*,*N*-dimethylformamide (DMF)

Scheme 2



to catalyze the transsilylation.[28] Polymers **1a**−**c** were prepared from the condensation of bis(chlorodimethylsilyl)hexane (**3**) with bis(trimethylsilyl)adipate (**5a**), bis(trimethylsilyl)terephthalate (**5b**), and bis(trimethylsilyl)isophthalate (**5c**), respectively (Scheme 1). The monomers employed for the preparation of poly(silyl ester)s **1a**−**c** are commercially available; however, the silyl chloride monomer, 1,6-bis(chlorodiisopropylsilyl)hexane (**4**), required for the synthesis of **2a-c**, was prepared according to Scheme 2. Attempts to prepare **4** by hydrosilylation chemistry, involving the reaction of chlorodiisopropylsilane with 1,5-hexadiene, failed to yield the disilylated product. Therefore, **4** was synthesized by the reaction of the Grignard reagent 1,6-bis(magnesium bromo)hexane with chlorodiisopropylsilane followed by chlorination of the crude product, 1,6-bis(diisopropylsilyl)hexane. Polymers **2a**−**c** were then prepared from the condensation of bis(chlorodiisopropylsilyl)hexane (**4**) with **5a**, **5b**, and **5c**, respectively

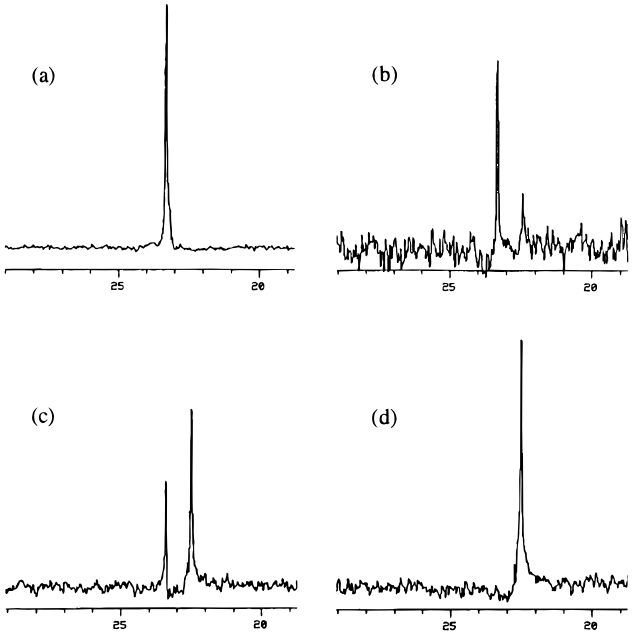


Figure 2. ^{29}Si NMR INEPT (THF-d_8) spectra monitoring the polymerization of **4** (^{29}Si δ at 35.9 ppm, not shown) with **5a** (^{29}Si δ at 23.3 ppm) to yield polymer **2a** (^{29}Si δ at 22.5 ppm). As the polymerization proceeds, the ^{29}Si resonances for **4** and **5a** reduce in intensity, while the ^{29}Si resonance of **2a** appears and increases in intensity: (a) 1 h; (b) 4 days; (c) 7 days, and (d) 11 days.

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

polymer	M_w (g/mol)	PDI	DP_w	T_g (°C)	T_m (°C)	^{29}Si NMR δ (ppm)
1a	9760	3.9	34	−62		23.5
1b	11400	2.5	30	−16	104	25.3
1c	7050	2.7	18	−24		25.1
2a	5160	2.0	12	−82		22.5
2b	15600	2.5	33	−21		24.7
2c	10400	3.1	22	−23		25.0

(Scheme 1).

The polymerizations were monitored by both ^{29}Si NMR INEPT and size-exclusion chromatography (SEC). For example, as the molecular weight increased by SEC, the disappearance of the trimethylsilyl ester resonance of **5a** at 23.3 ppm, and the appearance of the resonance at 22.5 ppm for new silyl ester bonds of the polymer backbone of **2a**, were observed in the ^{29}Si NMR spectra (Figure 2). The relative chain growth rates of polymer chains grown from the bulky isopropyl-substituted monomer **4** were slower than those from the methyl-substituted monomer **3**. By SEC, typical molecular weights ranged from 5000 to 15000 Da (Table 1).

The characterization of each polymer included infrared (IR), ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR INEPT spectroscopies, SEC, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The IR spectra of each of the polymers contain absorbances at frequencies corresponding to a Si−O stretch between 1000 and 1100 cm^{-1}, a Si−CH_3 stretch at approximately 1250 cm^{-1} for **1a**−**c** or a Si−CH stretch at approximately 1200 cm^{-1} for **2a**−**c**, a C−O stretch at 1250−1350 cm^{-1}, a strong carbonyl absorption at approximately 1700 cm^{-1}, and C−H stretches between 2800 and 3000 cm^{-1}. The expected absorbance for aromatic C−H stretches (>3000 cm^{-1}) can be discerned for **1b**−**c**, but it is not observed for **2b**−**c**, because of the overwhelming sp^3 C−H stretches from the isopropyl side chain substituents.

Table 2. Molecular Weight Data (M_w from SEC Based upon Polystyrene Standards) for the Degradation Studies of Poly(silyl ester)s 1a−c as Solutions in (i) THF Exposed to Atmospheric Water; (ii) 1% *tert*-Butyl Alcohol/THF, and (iii) 1% Methanol/THF

	1a		**1b**			**1c**		
time	ii	iii	i	ii	iii	i	ii	iii
5 min	9760	2090	11400	11400	9690	7040	7020	6470
1 h	6360	350	5830	6170	3990	4710	4730	2160
4 h	3320		3150	2310	1620	3120	2400	960
8 h	1700		2220	1350	920	2590	1710	650
24 h	790		1350	710	590	1070	720	
48 h	510		700			760	690	

Glass-transition temperatures (T_g) of the poly(silyl ester)s were measured by DSC under N_2, and the data are presented in Table 1. Each of the poly(silyl ester)s exhibited a T_g well-below room temperature, and the data correlate well with the chemical structures. In addition to the glass transition, a melting transition (T_m) at 104 °C was observed for **1b**, indicating crystallinity within the polymer bulk at room temperature.

The thermal stabilities of the poly(silyl ester)s were evaluated by TGA from 25 to 500 °C in air. Each of the six polymers showed no mass loss up to 190 °C. The polymers **1a**−**c** experienced approximately a 90% mass loss in one decomposition step by 500 °C, with the initial mass loss beginning at approximately 200 °C. In contrast, **2a**−**c** were found to be much more stable toward thermal degradation, exhibiting two distinct mass loss steps in the TGA spectra and approximately 45% of the mass remaining at 500 °C.

Factors that influence the stability of silyl esters toward nucleophilic degradation include the steric and electronic effects of the substituents on the silicon atoms, the nature of the nucleophile, and the solvent.[29] Since the nucleophilic attack can occur at either the silicon atom or at the carbonyl carbon, changing the steric hindrance around the silicon changes the amount and rate of cleavage by attack upon silicon. For poly(silyl ester)s, the composition and physical properties of the polymer backbone are additional factors that influence the degradative properties through the effects of hydrophobicity, solubility, chain rigidity, and crystallinity.

The degradation studies by hydrolysis and alcoholysis was initially performed upon the poly(silyl ester)s as solutions in THF in the presence of atmospheric water, added methanol, or added *tert*-butyl alcohol, so that the inherent stability of the polymers could be evaluated without the interference of physical effects. The decreasing molecular weights of the polymers over time were observed through SEC analysis (Tables 2 and 3 and Figure 3). Each of the polymers exhibited greater stability toward the *tert*-butyl alcohol than toward the methanol. The substituents attached to the silicon atoms greatly affected the relative degradation rates. The methyl-substituted poly(silyl ester)s were substantially less stable than the sterically bulky isopropyl-substituted polymers toward nucleophilic attack: the methyl-substituted polymers degraded into small molecules having a molecular weight less than 800 Da within 2 days in the presence of *tert*-butyl alcohol, while the isopropyl-substituted polymers with comparable molecular weights (**2b** and **2c**) required more than 10 days to degrade into the small molecules having molecular weights less than 1500 Da. The incorporation of aromatic repeat units into the polymer backbone

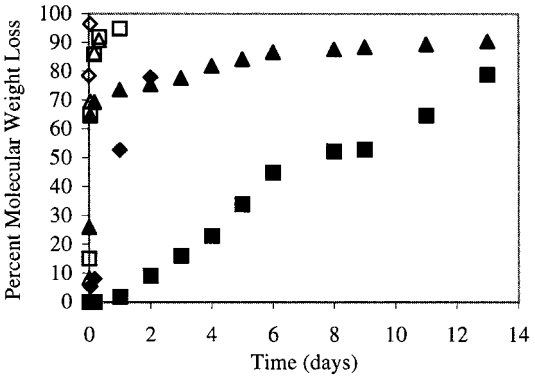


Figure 3. Plot of percentage molecular weight loss vs time for comparison of the relative rates of degradation of the poly(silyl ester)s: ◇, **1a**; □, **1b**; △, **1c**; ◆, **2a**; ■, **2b**; ▲, **2c** in 1% methanol/THF. In each case, an excess of methanol is present.

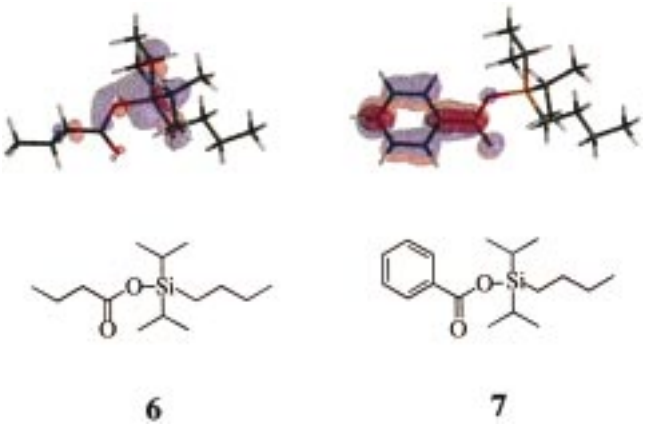
Table 3. Molecular Weight Data (M_w from SEC Based upon Polystyrene Standards) for the Degradation Studies of Poly(silyl ester)s 2a−c as Solutions in (i) THF Exposed to Atmospheric Water; (ii) 1% *tert*-Butyl Alcohol/THF, and (iii) 1% Methanol/THF

	2a			**2b**			**2c**		
time	i	ii	iii	i	ii	iii	i	ii	iii
5 min	4880	4860	4860	11600	11600	11600	10400	7910	7710
1 h	4860	4750	4620	11600	11600	11600	5240	4230	3680
4 h	4660	4650	4490	11600	11600	11600	3470	3400	3190
1 days	4150	3740	2310	11400	11200	11400	2960	2900	2750
2 days	2250	2000	1080	10980	10900	10540	2690	2640	2560
3 days	1210	1060		10700	10700	9740	2440	2390	2330
4 days				10650	10500	8940	2170	1790	1890
5 days				8730	8290	7670	1990	1600	1640
6 days				6810	6580	6400	1820	1420	1390
8 days				5980	5200	5540	1540	1350	1280
9 days				5770	4680	5470	1390	1300	1210
11 days				4990	4250	4090	1230	1150	1100
13 days				3490	2750	2460	1200	1120	1100

increased the stability of the polymer toward nucleophilic attack. For the series **2a**−**c**, **2b** was found to be the most stable toward nucleophilic attack. The relatively lower stability of **2c** in comparison to that of **2b** is presumably because the silicon atoms beside the *m*-phenylene group are sterically more accessible.

To better understand the difference in degradation between the alkyl- and aryl-based polymers, PM3 molecular orbital (MO) calculations were performed upon the model compounds **6** and **7**. The lowest unoccupied molecular orbital (LUMO) of **6** resides to a large extent upon the silicon of the silyl ester functionality, whereas the LUMO of **7** is located at the carbonyl and throughout the aromatic ring (Figure 4). This indicates that nucleophilic attack upon the silicon of **6** should occur more readily than attack upon the silicon of **7**, thereby agreeing with the decreased stability of polymer **1a**, in comparison to **1b** and **1c**, and of polymer **2a**, in comparison to **2b** and **2c**. Experimental determination of the site of nucleophilic attack (at the silicon vs the carbonyl) and higher level calculations are in progress.

Degradation studies of the poly(silyl ester)s as neat samples exposed to the lab environment (ca. 20 °C and 40% humidity) were then performed (Table 4). Both SEC and ^{29}Si NMR INEPT were employed to monitor the degradation. The degradation of methyl-substituted polymers gave 1,6-bis(dimethylhydroxysilyl)hexane as the hydrolysis product, which quickly condensed to form poly(1,6-dimethylsilylhexylene siloxane), observed in the SEC as the persistence of the polymer along with the production of small molecules. This was confirmed by



6 **7**

Figure 4. PM3 molecular orbital calculations showing the LUMO's of model alkyl and aryl silyl esters **6** and **7**.

Table 4. Molecular Weight Data (M_w from SEC Based upon Polystyrene Standards) for the Degradation Studies of the Poly(silyl ester)s as Solids in Air at ca. 20 °C and 40% Humidity

time	**1b**	**1c**	**2b**	**2c**
5 min	11400	7040	15000	10400
1 h	9510	5070	13900	4550
4 h	5710	5730	13400	4250
8 h	7260	9000	12800	3950
1 days	9850	12300	12200	3310
4 days			11400	2990
6 days			10300	2890
8 days			10100	2590
10 days			9560	2360
15 days			2100	2180
25 days			1080	

^{29}Si NMR INEPT (Figure 4), as changes in the ^{29}Si chemical shift from 25 ppm for silyl ester to 11 ppm for silanol, and finally to 8 ppm for siloxane. However, the degradation of **2a**−**c** gave small molecules after more than 20-days' exposure, without condensation.

A specific study of the hydrolysis of 1,6-bis(chlorodimethylsilyl)hexane, **3**, and 1,6-bis(chlorodiisopropylsilyl)hexane, **4**, followed by in situ polymerization demonstrated that at the same reaction conditions (80 °C, excess water), **3** formed a polymer with a molecular weight as large as 18000 Da in 3 h, whereas **4** formed an oligomer with a molecular weight less than 1500 after 4 days (Scheme 3). While the methyl-substituted silanol can easily condense to form a poly(ene-siloxane), the sterically bulky isopropyl groups attached to the silicon atoms inhibit the condensation, which account for the difference in the degradation products from the poly(silyl ester)s of **1a**−**c** versus **2a**−**c** in the solid state.

Interestingly, although there is little difference between the degradation rates of **1b** and **1c** in solution, ^{29}Si NMR INEPT showed that as solids, the relative stability of **1b** is higher than that of **1c** (Figure 5). While most silyl ester bonds in **1c** had decomposed and condensed to form poly(ene-siloxane) after 4 h of exposure to the laboratory atmosphere, there was still 30% of the silyl ester bonds remaining in **1b** after 8 h. DSC analysis revealed that the improved stability for **1b** in the solid state was due to crystallinity (both a normal glass transition at −16 °C and a melting transition at 104 °C were observed for **1b**). However, in solution, the entire polymers are dissolved and homogeneously dispersed, and the stability is not affected by crystallinity.

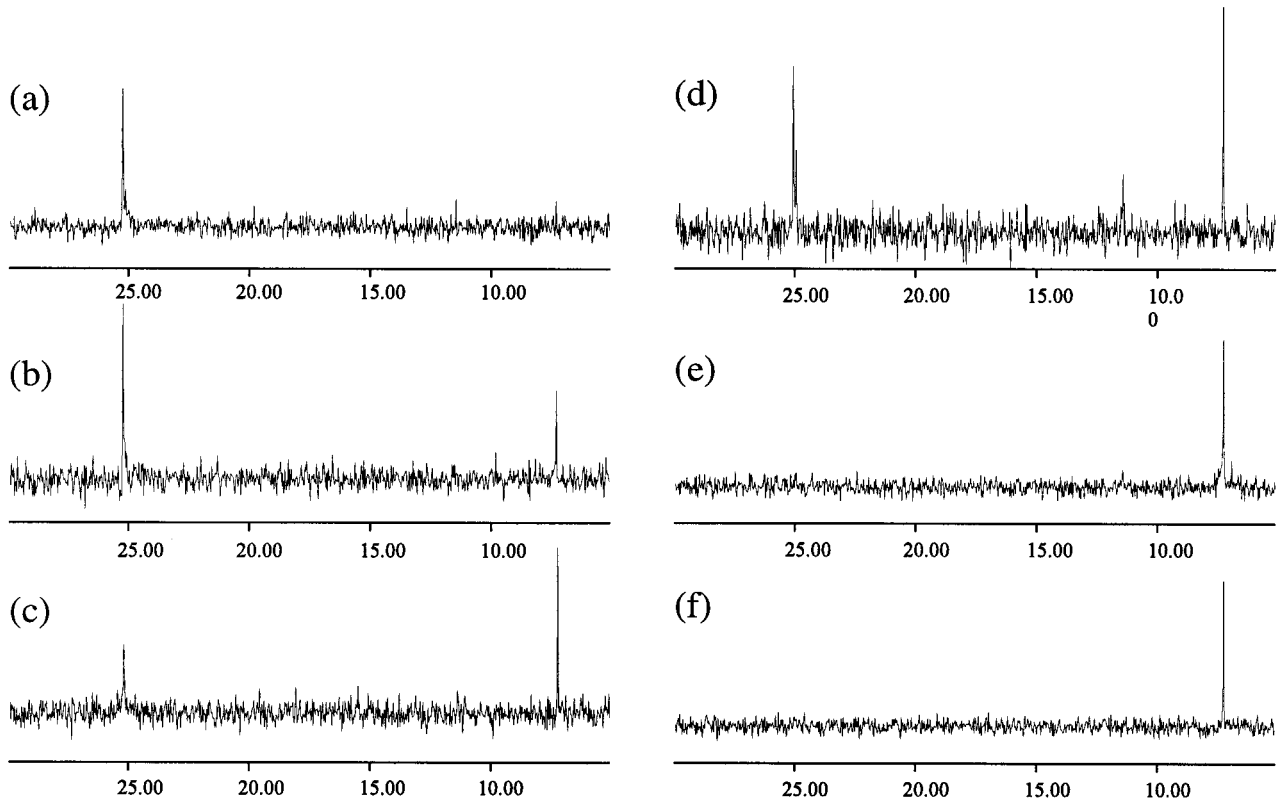
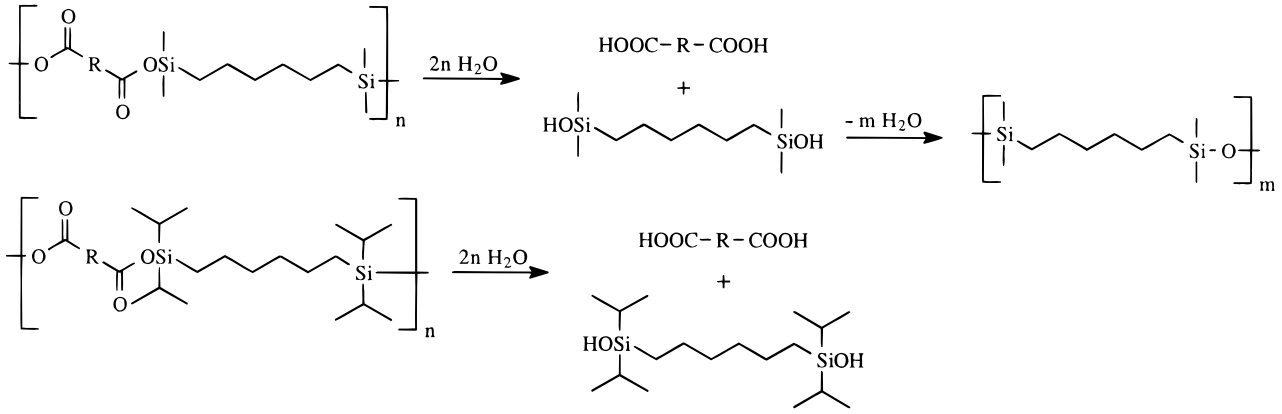


Figure 5. ^{29}Si NMR INEPT (THF-d_8) spectra monitoring the degradation of polymers **1b** and **1c** as solid samples in air exposed to ca. 40% humidity at 20 °C, demonstrating the increased stability toward hydrolytic cleavage for crystalline **1b** in comparison to amorphous **1c**: (a) **1b** after 1 h, (b) **1b** after 4 h, (c) **1b** after 8 h, (d) **1c** after 1h, (e) **1c** after 4 h, and (f) **1c** after 8 h.

Scheme 3



Conclusions

Incorporation of trialkyl-substituted silyl ester linkages with isopropyl side groups allowed for the extension of the hydrolytic stabilities of poly(silyl ester)s and the generation of such materials exhibiting the greatest resistance to cleavage thus far. To evaluate the extent of nucleophilic attack at silicon versus the carbonyl carbon of the silyl ester linkages as a function of the nucleophilic agent and reaction conditions, we have progressed with mechanistic studies employing isotope-labeled nucleophiles. The experimental mechanistic findings will be compared with theoretical calculations, which are expected to lead to further design of advanced poly(silyl ester)s with larger breadths of hydrolytic degradation properties. Applications such as matrices for drug release, temporary coatings, temporary adhesives, or other purposes are envisioned.

Experimental Section

General Directions. All manipulations of reagents and reactions were performed under argon on a double manifold, 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 the standard. ^{13}C NMR spectra were recorded at 75 MHz on a Varian Unity-plus spectrometer with the solvent carbon signal as the standard. ^{29}Si NMR spectra were recorded using standard INEPT (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; data analysis was performed with Trisec SEC Software, version 3.00 (Viscotek Corp., Houston, TX). Two 5-μm Polymer Laboratories PL$_{gel}$ columns (300 × 7.7 mm^2)

connected in series in order of increasing pore size (500 Å, mixed bed C) were used with THF distilled from calcium hydride as the eluent. Molecular weights were based on polystyrene standards (Polymer Laboratories Ltd., Amherst, MA). Glass-transition temperatures were measured by differential scanning calorimetry under N_2, on a Perkin-Elmer DSC 4 differential scanning calorimeter. Heating rates were 10 °C/min up to 150 °C. T_g was taken as the midpoint of the inflection tangent. Thermogravimetric analyses were done in air, on a Perkin-Elmer TGS-2 thermogravimetric analyzer. For both DSC and TGA, the Perkin-Elmer instruments were upgraded with Instrument Specialists, Inc. (Antioch, IL) temperature program interface-PE, and data were acquired and analyzed using TA-PC software version 2.11a (Instrument Specialists, Inc.). Elemental analyses were performed by MHW Laboratories (Phoenix, AZ) and are reported for unpurified polymers. Calculations of theoretical elemental percentages are based upon the M_n of the polymers, the composition of the repeat units, and the contribution from the end group ($-Si(CH_3)_3$ and $-Cl$) using the following equation: Theoretical C% = $[(M_n - 108.64) \times$ C% in repeating unit + 36.03$]/M_n$, where 108.64 is the molecular weight of TMSCl and 36.03 is the mass of carbons present in the TMS end group; theoretical H% = $[(M_n - 108.64) \times$ H% in repeating unit + 9.07$]/M_n$, where 108.64 is the molecular weight of TMSCl and 9.07 is the mass of hydrogens present in the TMS end group. MO calculations were carried out with the PM3 method using the Spartan program (version 5.0) on an SGI Indigo RS5000 Workstation.

Materials. 1,6-bis(chlorodimethylsilyl)hexane and chlorodiisopropylsilane were purchased from United Chemical Technologies (Bristol, PA) and distilled prior to use. Adipic acid, terephthalic acid, isophthalic acid, 1,6-dibromohexane, 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*-butyl alcohol were obtained from Fisher Scientific and distilled from sodium. Chlorine gas (99.5+%) was purchased in a lecture bottle from Aldrich Co.; a saturated solution of Cl_2 in CCl_4 was prepared by bubbling Cl_2 into CCl_4, with the excess Cl_2 passing through a drying tube into a solution of $NaOH_{(aq)}$.

Bis(trimethylsilyl)terephthalate. To a solution of terephthalic acid (9.98 g, 0.0601 mol) in THF (100 mL) was added HMDS (20 mL, 0.095 mol) with stirring under argon. The reaction was heated at reflux for 4 h, the solvent and excess HMDS were removed under reduced pressure, and the product was isolated by distillation (129−130 °C, 0.1 mmHg) as a white solid (16.90 g, 0.05443 mol): yield 91%. IR (NaCl): 3150−3000, 2966, 2910, 1693, 1408, 1288, 1124, 858 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.38 (s, 18H, $-Si(CH_3)_3$), 8.06 (s, 4H, Ar) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ −0.29 ($-Si(CH_3)_3$), 130.68 (Ar***C***), 136.13 (Ar***C***), 166.06 (carbonyl ***C***) ppm. ^{29}Si NMR INEPT (59.6 MHz, $CDCl_3$): δ 25.1 ppm.

Bis(trimethylsilyl)isophthalate. To a solution of isophthalic acid (11.99 g, 0.07217 mol) in THF (100 mL) was added HMDS (20 mL, 0.095 mol) with stirring under argon. The reaction was heated at reflux for 4 h, the solvent and excess HMDS were removed under reduced pressure, and the product was isolated by distillation (119−120 °C, 0.1 mmHg) as a white solid (20.9 g, 0.0673 mol): yield 93%. IR (NaCl): 3150−3000, 2974, 2910, 1696, 1329, 1256, 1142, 1073, 859 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.38 (s, 18H, $-Si(CH_3)_3$), 7.48 (t, $J_1 = 8$ Hz, 1H, Ar), 8.18 (dd, $J_1 = 8$ Hz, $J_2 = 2$ Hz, 2H, Ar), 8.65 (t, $J_2 = 2$ Hz, 1H, Ar) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ −0.29 ($-Si(CH_3)_3$), 128.35 (Ar***C***), 131.67(Ar***C***), 131.77(Ar***C***), 134.25(Ar***C***), 165.82 (carbonyl***C***) ppm. ^{29}Si NMR INEPT (59.6 MHz, $CDCl_3$): δ 25.7 ppm.

1,6-Bis(chlorodiisopropylsilyl)hexane. In a 100-mL three-necked flask was prepared a Grignard reagent from 1,6-dibromohexane (12.65 g, 0.05186 mol) and magnesium (2.53 g, 0.104 mol) in diethyl ether (50 mL, freshly distilled from sodium). To the stirred solution was added dropwise over a 30-min period chlorodiisopropylsilane (15.63 g, 0.1037 mol) diluted with diethyl ether (25 mL). The mixture was then heated at reflux for 6 h under argon. The resulting solution was washed with 10% HCl, extracted with ether, dried over anhydrous sodium sulfate, and the ether removed in vacuo. A saturated solution of Cl_2 in CCl_4 (ca. 100 mL) at room temperature was then added dropwise to the crude 1,6-bis(diisopropylsilyl)hexane under exclusion of moisture until the reaction mixture remained yellow. During this chlorination procedure, HCl was vigorously evolved. The solvent was removed in vacuo and the product isolated with Kugelrohr distillation (175 °C, 0.1 mmHg) as a colorless oil (13.59 g, 0.03543 mol): yield 68%. IR (NaCl): 3000−2860, 1464, 1280, 1200, 1075, 1000, 883 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.79 (t, 4H, $J = 7$ Hz, $-CH_2CH_2CH_2CH_2CH_2CH_2-$), 1.05 (d, 24H, $J = 7$ Hz, $-CH(CH_3)_2$), 1.08 (m, 4H, $-CH(CH_3)_2$), 1.24 (m, 4H, $-CH_2CH_2CH_2CH_2CH_2CH_2-$), 1.35 (m, 4H, $-CH_2CH_2CH_2CH_2CH_2CH_2-$) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 12.78 ($-CH_2CH_2CH_2CH_2CH_2CH_2-$), 14.09 ($-CH(CH_3)_2$), 17.26 ($-CH(CH_3)_2$), 23.17 ($-CH_2CH_2CH_2CH_2CH_2CH_2-$), 32.89 ($-CH_2CH_2CH_2CH_2CH_2CH_2-$) ppm. ^{29}Si NMR INEPT (59.6 MHz, $CDCl_3$): δ 35.9 ppm.

General Procedure for the Synthesis of Poly(silyl ester)s. The appropriate bis(trimethylsilyl) ester was distilled into a tared reaction tube. To the reaction tube was then added 1 equiv of the appropriate 1,6-bis(chlorosilyl)hexane (freshly distilled under argon) via a tared flame-dried syringe. About 10 mol % *N,N*-dimethylformamide (distilled from CaO) was then added via syringe. The reaction was typically allowed to proceed with stirring under an argon atmosphere at 100 °C for 10−20 days. Because of the hydrolytic instabilities of the polymers, purification involved only evacuation (0.1 mmHg) of the reaction tube at room temperature for 6 h to remove any remaining DMF.

Poly[bis(dimethylsilyl)hexylene adipate] (1a). This polymer was prepared according to the published procedure.[24]

Poly[bis(dimethylsilyl)hexylene terephthalate] (1b). This was prepared from the reaction of **5b** (0.9809 g, 3.159 mmol) with **3** (0.8573 g, 3.159 mmol) at 100 °C for 8 days. $T_g = -16$ °C. IR (NaCl): 3150−3000, 2925, 1695, 1590, 1510, 1425, 1287, 1253, 1114, 1106, 1064, 1057, 1020, 881, 842 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.34 (s, 12H, $-Si(CH_3)_2-$), 0.86 [br m, 4H, $-(Si(CH_3)_2CH_2CH_2CH_2)_2$], 1.33 [br m, 4H, $-(Si(CH_3)_2CH_2CH_2CH_2)_2$], 1.38 [br m, 4H, $-(Si(CH_3)_2CH_2CH_2CH_2)_2$], 8.03 (s, 4H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.77 [$-(Si(CH_3)_2-$], 16.71 [$-(Si(CH_3)_2CH_2CH_2CH_2)_2$], 23.69 [$-(Si(CH_3)_2CH_2CH_2CH_2)_2$], 33.76 [$-(Si(CH_3)_2CH_2CH_2CH_2)_2$], 130.71 (Ar***C***), 136.18 (Ar***C***), 166.01 (carbonyl***C***) ppm. ^{29}Si NMR INEPT (59.6 MHz, $CDCl_3$): δ 25.3 ppm. $M_w = 11400$ g/mol; $M_w/M_n = 2.5$, based upon SEC with polystyrene standards. Anal. Calcd. for $(C_{18}H_{28}O_4Si_2)_n$, $(364.59)_n$, $M_n = 4560$: C, 58.67%; H, 7.76%. Found: C, 57.54%; H, 8.05%.

Poly[bis(dimethylsilyl)hexylene isophthalate] (1c). This was prepared from the reaction of **5c** (0.6433 g, 2.072 mmol) with **3** (0.5618 g, 2.070 mmol) at 100 °C for 9 days. $T_g = -24$ °C. IR (NaCl): 3150−3000, 3000−2860, 1702, 1600, 1461, 1322, 1290, 1255, 1144, 1095, 1074, 915, 849, 750 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.34 (s, 12H, $-Si(CH_3)_2-$), 0.87 [br m, 4H, $-(Si(CH_3)_2CH_2CH_2CH_2)_2$], 1.33 [br m, 4H, $-(Si(CH_3)_2CH_2CH_2CH_2)_2$], 1.38 [br m, 4H, $-(Si(CH_3)_2CH_2CH_2CH_2)_2$], 7.50 (br m, 1H, Ar), 8.17 (br m, 2H, Ar), 8.60 (br m, 1H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ −1.73 [$-(Si(CH_3)_2-$], 16.76 [$-(Si(CH_3)_2CH_2CH_2CH_2)_2$], 23.70 [$-(Si(CH_3)_2CH_2CH_2CH_2)_2$], 33.80 [$-(Si(CH_3)_2CH_2CH_2CH_2)_2$], 129.41 (Ar***C***), 132.32 (Ar***C***), 132.84 (Ar***C***), 134.94 (Ar***C***), 165.97 (carbonyl***C***) ppm. ^{29}Si NMR INEPT (59.6 MHz, $CDCl_3$): δ 25.1 ppm. $M_w = 7050$ g/mol; $M_w/M_n = 2.7$, based upon SEC with polystyrene standards. Anal. Calcd. for $(C_{18}H_{28}O_4Si_2)_n$, $(364.59)_n$, $M_n = 2610$: C, 58.22%; H, 7.77%. Found: C, 58.12%; H, 8.05%.

Poly[bis(diisopropylsilyl)hexylene adipate] (2a). This was prepared from the reaction of **5a** (0.6145 g, 2.115 mmol) with **4** (0.8114 g, 2.115 mmol) at 100 °C for 21 days. $T_g = -82$ °C. IR (NaCl): 3000−2860, 1718, 1701, 1464, 1458, 1368, 1260, 1187, 1010, 883 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.78 [br m, 4H, $-(Si(C_3H_7)_2CH_2CH_2CH_2)_2$], 1.02 [br m, 24H,

$-Si(CH(CH_3)_2)_2-$], 1.14 [br m, 4H, $-Si(CH(CH_3)_2)_2-$], 1.23 [br m, 4H, $-(Si(C_3H_7)_2CH_2CH_2CH_2CH_2)_2$], 1.29 [br m, 4H, $-(Si(C_3H_7)_2CH_2CH_2CH_2)_2$], 1.63 [br m, 4H, $-(COCH_2CH_2)_2$], 2.33 [br m, 4H, $-(COCH_2CH_2)_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.26 [$-(Si(C_3H_7)_2CH_2CH_2CH_2)_2$], 17.20 [$-Si(CH(CH_3)_2)_2-$], 17.39 [$-Si(CH(CH_3)_2)_2-$], 23.09 [$-(Si(C_3H_7)_2CH_2CH_2CH_2)_2$], 24.65 [$-(COCH_2CH_2)_2$], 33.20 [$-(Si(C_3H_7)_2CH_2CH_2CH_2CH_2)_2$], 35.51 [$-(COCH_2CH_2)_2$], 172.94 (carbonyl***C***) ppm. ^{29}Si NMR INEPT (59.6 MHz, $CDCl_3$): δ 22.5 ppm. $M_w = 5160$ g/mol; $M_w/M_n = 2.0$, based upon SEC with polystyrene standards. Anal. Calcd. for $(C_{24}H_{48}O_4Si_2)_n$, $(456.81)_n$, $M_n = 2580$: C, 61.84%; H, 10.49%. Found: C, 61.16%; H, 10.46%.

Poly[bis(diisopropylsilyl)hexylene terephthalate] (2b). This was prepared from the reaction of **5b** (0.9934 g, 3.199 mmol) with **4** (1.227 g, 3.199 mmol) at 100 °C for 18 days. $T_g = -21$ °C. IR (NaCl): (aromatic C−H stretch is too small to observe), 3000−2860, 1704, 1585, 1461, 1298, 1220, 1119, 1102, 1020, 830 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.92 [br m 4H, $-(Si(C_3H_7)_2CH_2CH_2CH_2)_2$], 1.08 [br m, 24H, $-Si(CH(CH_3)_2)_2-$], 1.27 [br m, 4H, $-Si(CH(CH_3)_2)_2-$], 1.32 [br m, 4H, $-(Si(C_3H_7)_2CH_2CH_2CH_2)_2$], 1.36 [br m, 4H, $-(Si(C_3H_7)_2CH_2CH_2CH_2CH_2)_2$], 8.08 (s, 4H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.76 [$-(Si(C_3H_7)_2CH_2CH_2CH_2)_2$], 12.38 [$-Si(CH(CH_3)_2)_2-$], 17.43 [$-Si(CH(CH_3)_2)_2-$], 23.03 [$-(Si(C_3H_7)_2CH_2CH_2CH_2)_2$], 33.07 [$-(Si(C_3H_7)_2CH_2CH_2CH_2)_2$], 130.01 (Ar***C***), 135.16 (Ar***C***), 165.51 (carbonyl***C***) ppm. ^{29}Si NMR INEPT (59.6 MHz, $CDCl_3$): δ 24.7 ppm. $M_w = 15600$ g/mol; $M_w/M_n = 2.5$, based upon SEC with polystyrene standards. Anal. Calcd. for $(C_{26}H_{44}O_4Si_2)_n$, $(476.79)_n$, $M_n = 6240$: C, 64.94%; H, 9.28%. Found: C, 64.08%; H, 9.16%.

Poly[bis(diisopropylsilyl)hexylene isophthalate] (2c). This was prepared from the reaction of **5c** (0.8101 g, 2.609 mmol) with **4** (1.001 g, 2.609 mmol) at 100 °C for 18 days. $T_g = -23$ °C. IR (NaCl): (aromatic C−H stretch is too small to observe), 3000−2860, 1705, 1601, 1463, 1321, 1290, 1257, 1142, 890, 775 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.01 [br m 4H, $-(Si(C_3H_7)_2CH_2CH_2CH_2)_2$], 1.14 [br m, 24H, $-Si(CH(CH_3)_2)_2-$], 1.29 [br m, 4H, $-Si(CH(CH_3)_2)_2-$], 1.33 [br m, 4H, $-(Si(C_3H_7)_2CH_2CH_2CH_2)_2$], 1.41 [br m, 4H, $-(Si(C_3H_7)_2CH_2CH_2CH_2CH_2)_2$], 7.57 (br m, 1H, Ar), 8.23 (br m, 2H, Ar), 8.69 (br m, 1H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.65 [$-(Si(C_3H_7)_2CH_2CH_2CH_2)_2$], 13.39 [$-Si(CH(CH_3)_2)_2-$], 17.65 [$-Si(CH(CH_3)_2)_2-$], 24.02 [$-(Si(C_3H_7)_2CH_2CH_2CH_2)_2$], 34.04 [$-(Si(C_3H_7)_2CH_2CH_2CH_2)_2$], 129.57 (Ar***C***), 132.27 (Ar***C***), 132.92 (Ar***C***), 135.03 (Ar***C***), 165.75 (carbonyl***C***) ppm. ^{29}Si NMR INEPT (59.6 MHz, $CDCl_3$): δ 25.0 ppm. $M_w = 10400$ g/mol; $M_w/M_n = 3.1$, based upon SEC with polystyrene standards. Anal. Calcd. for $(C_{26}H_{44}O_4Si_2)_n$, $(476.79)_n$, $M_n = 3360$: C, 65.49%; H, 9.30%. Found: C, 59.95%; H, 8.38%.

Degradation of Polymers in Solution. Approximately 10 mg of the polymer was dissolved in 2 mL of THF. Exposure to the laboratory atmosphere (ca. 20 °C, 40% humidity) provided for degradation by water. For degradation by the alcoholic agents, methanol (0.02 mL, 1%) or *tert*-butyl alcohol (0.02 mL, 1%) was added to the solution of the polymer in a closed vial. At the appropriate times (5 min, 1 h, 4 h, 8 h, 1 d, 2 d, etc.), 0.1 mL of the polymer solution was injected into the SEC and the resulting chromatogram was analyzed.

Degradation of Polymers as Solid Samples in Air. Eight samples of approximately 10 mg each of the polymer were placed into individual glass vials. The vials were open to the laboratory environment that was approximately 20 °C and 40% humidity. At the appropriate times (5 min, 1 h, 4 h, 8 h, 1 d, 2 d, etc.), the polymer samples were dissolved in THF-d_8 and the ^1H NMR spectra, ^{29}Si INEPT NMR spectra, and SEC chromatograms were obtained.

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