Linear and Hyperbranched Poly(silyl ester)s: Synthesis via Cross-Dehydrocoupling-Based Polymerization, Hydrolytic Degradation Properties, and Morphological Analysis by Atomic Force Microscopy

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ABSTRACT: Poly(silyl ester)s with differing compositions and architectures were synthesized via cross-dehydrocoupling polymerizations of AB and AB_2 monomers. Three poly(silyl ester)s—linear poly(dimethylsilyl benzoate), linear poly(diisopropylsilyl benzoate), and hyperbranched poly(dimethylsilyl benzoate)—were synthesized through the dehydrocoupling polymerization of 4-(dimethylsilyl)benzoic acid, 4-(diisopropylsilyl)benzoic acid, and 3,5-bis(dimethylsilyl)benzoic acid, respectively, as 10 M solutions in ethylene glycol diethyl ether in the presence of 0.25 mol % of 10 wt % palladium on activated carbon at 100 °C under argon for 1−3 days. The characterization of each polymer included infrared (IR), ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR INEPT spectroscopies, size exclusion chromatography (SEC), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The degree of branching of hyperbranched poly(dimethylsilyl benzoate) was 51%, as determined by ^{1}H NMR spectroscopy, with spectral analysis confirmed through comparison with model compounds. The hydrolytic degradation properties of the polymers in solution and in the solid state were studied quantitatively by monitoring the molecular weight reduction over time using SEC. In addition, the erosion processes of solvent-cast polymer films upon hydrolytic degradation were investigated by monitoring the changes in the surface topographies and morphologies using atomic force microscopy (AFM). The rate of polymer degradation was reduced for the isopropyl-substituted silyl ester linkages in comparison to those bearing methyl silicon side chain substituents. Hydrolysis of each of the linear polymers gave smooth molecular weight loss over time, whereas the hyperbranched material exhibited a two-stage degradation profile.

Introduction

Degradable polymers serve important functions as temporary materials for performance as matrices or structural components for applications in biomedical or agricultural areas and for reduction of the impact of synthetic functional materials upon the environment.[1−6] Significant efforts have been focused upon the preparation and study of poly(ester)s,[1,4−11] poly(anhydride)s,[12−16] poly(ortho ester)s,[17−19] and poly(vinyl alcohol)s[20] as hydrolytically or biologically degradable materials. However, even with this large number of degradable polymers available, relatively long degradation times are typically required without the addition of catalytic excipients. Poly(silyl ester)s[21−26] have been recently reported as a new type of single-component homopolymeric degradable system upon nucleophilic attack with rapid and attunable degradation rates. In most cases, the times required for complete breakdown of poly(silyl ester)s to monomeric components are on the order of seconds to weeks. The degradation rates are dependent upon the steric and electronic effects of the substituents attached to the silyl ester linkages,[27,28] as well as the physical properties of the polymeric material, such as hydrophobicity, solubility, and crystallinity.[23]

Several synthetic routes have been developed to prepare poly(silyl ester)s, including transsilylation esterification of AA/BB comonomers,[22−24,26,29] transsilylation esterification of AB monomers,[25,29] and hydrosilylation of AB monomers.[25] In comparison to the polymerization through AA/BB comonomers, the use of an AB monomer avoids the difficulties associated with controlling the stoichiometric equivalences of reactive groups and has allowed for higher degrees of polymerization to be achieved. Each of the AB polymerizations employed for the preparation of poly(silyl ester)s has relied upon hydrosilylation chemistries: in the transsilylation route, the AB monomer was prepared by hydrosilylation; the hydrosilylation-based polymerization utilized the coupling of unsaturated carbon−carbon bonds with hydrosilanes to construct trialkylsilyl ester linkages along the polymer backbone. The complication in each of these systems is that the hydrosilylation reaction fails with sterically bulky hydrosilanes. Therefore, the polymerizations through AB monomers were limited to the synthesis of poly(silyl ester)s with methyl side chain substituents, and the polymers prepared were highly hydrolytically labile.[25] To attune further the degradation properties of poly(silyl ester)s via AB monomers and to improve the hydrolytic stability toward nucleophilic attack, we now report the synthesis of poly(silyl ester)s via cross-dehydrocoupling chemistry.[21]

In this work, the cross-dehydrocoupling route is also applied to the polymerization of AB_2 monomers to obtain degradable hyperbranched poly(silyl ester)s. In comparison to linear polymers, synthesized through the polymerization of AA/BB or AB monomers, an increasing amount of interest is being shown toward polymeric materials having hyperbranched architectures synthesized through the polymerization of AB_n monomers.[30−39] Hyperbranched polymers possess enhanced physical properties, such as high solubility and low viscosity, imparted by their near-globular shape, in comparison to their linear analogues.[40] The degree of branching[41−43] in hyperbranched polymers has been determined by

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controlled degradation;[44,45] however, little attention has been paid to the design and preparation of hyperbranched polymers for degradation aimed applications.[46,47] For hyperbranched polymers prepared from AB_2 monomers, the statistical degree of branching of 50% has been observed for many condensation-derived polymers. When these polymers are of high degrees of polymerization, a 50% degree of branching leads to ca. 25% of the monomeric repeat units being present as chain ends distributed throughout the macromolecular architecture. Therefore, cleavage of any one of 25% of the backbone linkages will release only a single monomeric unit, resulting in a minimal reduction in the overall polymer molecular weight. This is in contrast to linear polymer chains, which contain only two chain ends. It is then expected that hyperbranched degradable polymers should, in general, exhibit degradation behaviors that differ substantially from linear polymers. The architectural effects between linear and hyperbranched structures upon the degradation properties of polymeric materials are discussed. The erosion processes of the poly(silyl ester)s were evaluated by atomic force microscopy[48−51] (AFM) analysis, which monitored the nanoscale changes in surface topography of the eroding polymer films.

Results and Discussion

Although the transition-metal-catalyzed dehydrocoupling of hydrosilanes to afford poly(silane)s has been extensively studied over the past decade,[52,53] the construction of silyl ester linkages by catalytic cross-dehydrocoupling reactions of hydrosilanes with carboxylic acids was reported only recently by the group of Kawakami to produce poly(silyl ester)s via the polymerization of 1,4-bis(dimethylsilyl)benzene with adipic acid and terephthalic acid.[21] To apply the cross-dehydrocoupling chemistry to the preparation of poly(silyl ester)s via AB monomers, the monomers designed in this methodology contain a hydrosilyl group and a carboxylic acid group; these functionalities are stable in the presence of each other until a dehydrocoupling catalyst is added. This dehydrocoupling approach possesses the advantage over the transsilylation[29] and hydrosilylation[25] routes in that the AB monomers do not contain the highly reactive and moisture-sensitive silyl ester functionality, which significantly eliminates the technical difficulty in the purification and handling of monomers.

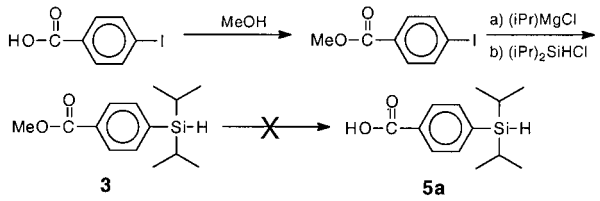
Before this dehydrocoupling approach was applied to the polymerization of monomers containing sterically bulky silicon substituents, a series of monofunctional small molecule model dehydrocoupling reactions were performed (Table 1). Dimethylphenylsilane (**1**) and diisopropylphenylsilane (**2**) were selected as model compounds for the hydrosilyl functionality of the monomers and growing polymer chain ends having different degrees of steric bulk around the silicon atoms. The silanes **1** and **2** were prepared by Grignard reactions between phenylmagnesium bromide and the corresponding chlorosilanes in tetrahydrofuran.[54] A number of Rh, Pd, and Pt catalysts were screened in this study, including carbonylchlorobis(triphenylphosphine)rhodium(I) {$[(C_6H_5)_3P]_2Rh(CO)Cl$}, carbonylchlorotris(triphenylphosphine)rhodium(I) {$[(C_6H_5)_3P]_3Rh(CO)Cl$}, palladium,[21] palladium hydroxide [$Pd(OH)_2$], platinum, *cis*-bis(benzonitrile)dichloroplatinum(II) [$(C_6H_5CN)_2PtCl_2$], and dichloro(1,5-cyclooctadiene)platinum(II) [$Pt(COD)Cl_2$]. The reactions of **1** and **2** with benzoic acid in the presence of each of these transition metal catalysts were monitored by ^{1}H NMR and ^{29}Si NMR INEPT. The results given in Table 1 demonstrate the effectiveness of the catalysts toward effecting the dehydrocoupling reaction. The high degree of conversion obtained with the Pd catalysts suggested the feasibility of the cross-dehydrocoupling reaction toward polymer formation. Of the catalysts listed above, $[(C_6H_5)_3P]_3Rh(CO)Cl$, Pt, $(C_6H_5CN)_2PtCl_2$, and $Pt(COD)Cl_2$ exhibited no catalytic activity for the dehydrocoupling reaction between **2** and benzoic acid. Pd and $Pd(OH)_2$ were found to be the most effective catalysts for **2**, whereby 100% conversion was achieved within 12 h in DMF at 100 °C, based upon the loss of starting materials and the formation of products determined by ^{1}H NMR and ^{29}Si NMR INEPT analysis. With the addition of 10 wt % Pd on activated carbon as the catalyst, the dehydrocoupling reaction between **1** and benzoic acid reached 100% conversion at room temperature within 4 h. Because of the presence of steric bulk around the silicon, the reaction rates for **2** were found to be substantially slower than those for **1**. Considering the possible cleavage of silyl ester linkages induced by the hydroxyl functional groups in $Pd(OH)_2$ upon lengthy reaction times at elevated temperatures, Pd was selected for use as the catalyst for the polymerization studies. In these model studies, *N*,*N*-dimethylformamide (DMF) was used as the solvent to allow the reaction temperature to reach above 100 °C. However, to avoid the possible transsilylation esterification side reactions catalyzed by DMF,[23,26,29] ethylene glycol diethyl ether and toluene were introduced as alternative high boiling point solvents for the dehydrocoupling polymerizations.

Table 1. Model Reactions Performed To Investigate the Dehydrocoupling Reactions of Dimethylphenylsilane, 1, and Diisopropylphenylsilane, 2, with Benzoic Acid under Argon for 12 h with 0.25 mol % Catalyst

silanes	catalyst	solvent	temp (°C)	conv[a] (%)
1[b]	Pd/C	THF	25	100[d]
2[c]	$(PPh_3)_2Rh(CO)Cl$	DMF	100	85[e]
2[c]	$(PPh_3)_3Rh(CO)Cl$	DMF	100	0[e]
2[c]	Pd/C	THF	65	33[e]
2[c]	Pd/C	DMF	100	100[e]
2[c]	$Pd(OH)_2$/C	DMF	100	100[e]
2[c]	Pt/C	DMF	100	0[e]
2[c]	$(PhCN)_2PtCl_2$	DMF	100	0[e]
2[c]	$Pt(COD)Cl_2$	DMF	100	0[e]

[a] The conversions were calculated based upon the loss of starting materials and the formation of products, as monitored by ^{1}H NMR and ^{29}Si NMR INEPT analysis. [b] ^{1}H δ of $(CH_3)_2PhSi\boldsymbol{H}$ at 4.58 ppm, ^{29}Si δ at −17.0 ppm. [c] ^{1}H δ of $(^iPr)_2PhSi\boldsymbol{H}$ at 4.00 ppm, ^{29}Si δ at 5.9 ppm. [d] ^{29}Si δ of $(CH_3)_2Ph\boldsymbol{Si}OCOPh$ at 13.1 ppm. [e] ^{29}Si δ of $(^iPr)_2Ph\boldsymbol{Si}OCOPh$ at 13.2 ppm.

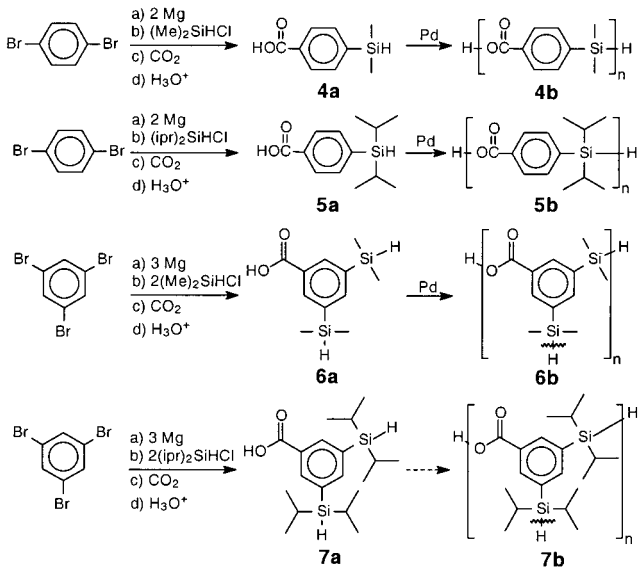
Scheme 1



Considering the possible cleavage of silyl ester linkages induced by the hydroxyl functional groups in $Pd(OH)_2$ upon lengthy reaction times at elevated temperatures, Pd was selected for use as the catalyst for the polymerization studies. In these model studies, *N*,*N*-dimethylformamide (DMF) was used as the solvent to allow the reaction temperature to reach above 100 °C. However, to avoid the possible transsilylation esterification side reactions catalyzed by DMF,[23,26,29] ethylene glycol diethyl ether and toluene were introduced as alternative high boiling point solvents for the dehydrocoupling polymerizations.

The synthesis of the AB monomers was initially proposed to be accomplished via three steps, including an esterification, a Grignard reaction,[55] and a hydrolysis reaction, starting with iodobenzoic acid (Scheme 1). After the protection of the carboxylic acid group by

Scheme 2



esterification, the iodine−magnesium exchange reaction between methyl 4-iodobenzoate and isopropylmagnesium chloride generated the functionalized arylmagnesium chloride,[56,57] which then underwent reaction with the electrophile, chlorodiisopropylsilane, to give the product **3** in 85% yield. However, conditions were not found that allowed for even the diisopropylsilane group to survive the hydrolysis of the methyl ester. An alternative route was then developed (Scheme 2). The monomers were synthesized via stepwise in-situ Grignard reactions[54,58] with chlorodialkylsilanes and CO_2, starting from 1,4-dibromobenzene for **4a** and **5a** and 1,3,5-tribromobenzene for **6a** and **7a**. Following the standard aqueous workup, the products were isolated by column chromatography and further purified by vacuum distillation, giving overall yields ranging from 15% to 40%.

Linear and hyperbranched poly(silyl ester)s were then prepared through the dehydrocoupling reactions of the AB and AB_2 monomers (Scheme 2). An addition of 0.25 mol % of 10 wt % Pd/C as the catalyst[21] was used in all polymerizations. Ethylene glycol diethyl ether and toluene were used as solvents with high boiling points and differing polarities. The typical reaction time for the polymerizations of **4a** and **6a** was 1 day, and the polymerization time for **5a** and **7a** was 3 days. A control study was performed upon the polymerization of **5a** to allow for the solvent and the concentration of reagents to be optimized to produce the poly(silyl ester)s with high molecular weights. Size exclusion chromatography (SEC) and NMR were employed to monitor the reactions. It was found that both the solvent and concentration were crucial components for the formation of polymers with high degrees of polymerization (Figure 1). Dehydrocoupling reactions occurred more rapidly in the polar solvent, ethylene glycol diethyl ether, than in the nonpolar solvent, toluene. At high dilution, high degrees of polymerization were not achieved, based upon SEC analysis. High concentrations promoted intermolecular reaction, yielding polymers with higher degrees of polymerization.

The polymerizations were monitored by ^{1}H NMR, ^{29}Si NMR INEPT (Figure 2), and SEC. As an example, at the late stage of the polymerization of **4a**: the resonance corresponding to the proton attached to

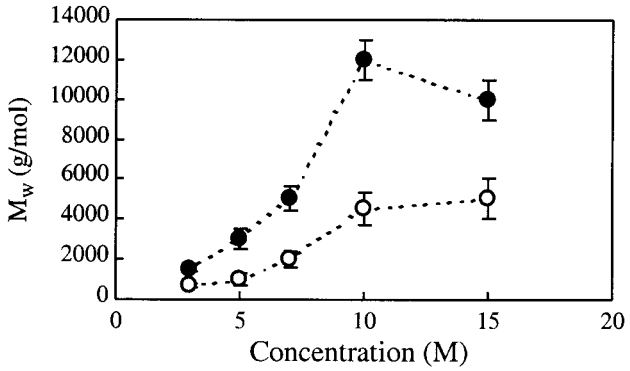


Figure 1. Evaluation of the effects of solvent and the concentration of reagents upon the polymerization of **5a**, as determined by measurement of M_w by SEC. The M_w values were measured after polymerization of **5a** at 100 °C for 3 days in the presence of 0.25 mol % of 10 wt % Pd/C as the catalyst: ○, in toluene; ●, in ethylene glycol diethyl ether. Values given are the average for the experiments repeated in triplicate, with the standard deviation as the error amount.

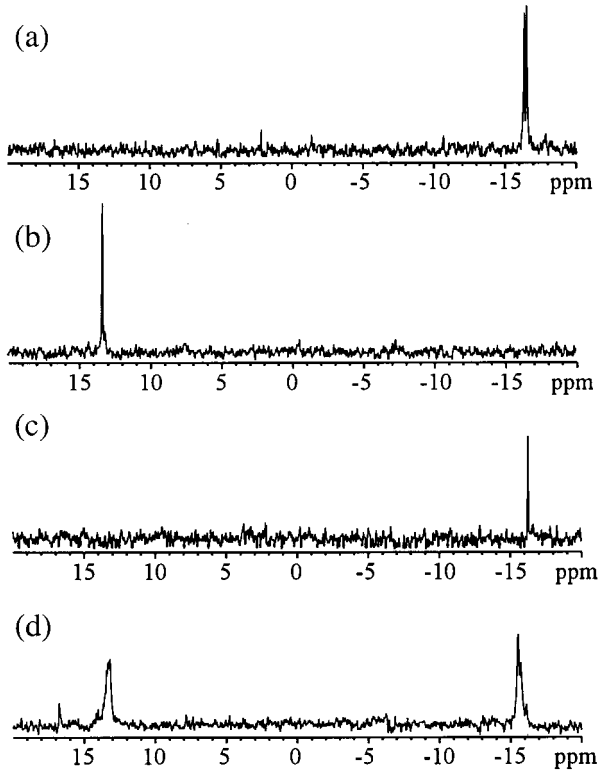


Figure 2. ^{29}Si NMR INEPT (59.6 MHz, $CDCl_3$) spectra of (a) **4a** (^{29}Si δ at −16.3 ppm), (b) **4b** (^{29}Si δ at 13.3 ppm), (c) **6a** (^{29}Si δ at −16.3 ppm), and (d) **6b** (^{29}Si δ at −16.3 and 13.2 ppm).

silicon at 4.5 ppm disappeared in the ^{1}H NMR spectrum; the dimethylhydrosilane ^{29}Si resonance of **4a** at −16.3 ppm was replaced by the resonance at 13.3 ppm for the silyl ester functionalities along the backbone of polymer **4b** in ^{29}Si NMR INEPT; and the formation of polymer with high molecular weight was observed through SEC analysis. The polymerization of the AB_2 monomer, **6a**, consumes only half of the hydrosilane functionalities; therefore, the single sharp resonance at −16.3 ppm for the dimethylhydrosilane functionality observed in the ^{29}Si NMR INEPT broadened as the silyl ester ^{29}Si resonance appeared as a broad peak centered at 13.2 ppm. In addition, the relative intensity of the hydrosilane proton resonance of **6b** reduced to half of the

Table 2. Characterization Data for the Poly(silyl ester)s

	M_w[a]	PDI	DP_w	T_g (°C)	^{29}Si NMR δ[b] (ppm)	$t_{1/2}$[c] (days)
4b	3 000	1.5	17	75	13.3	0.3
5b	12 000	2.3	51	89	13.6	6
6b	23 000	6.8	97	41	−16.3, 13.2	0.3

[a] M_w values were obtained from SEC and are based upon calibration with polystyrene standards. [b] In $CDCl_3$. [c] $t_{1/2}$ values are the half-lives of the polymers dissolved in THF and exposed to the laboratory environment (ca. 25 °C and 35% humidity). The $t_{1/2}$ value was taken as the time at which the polymer molecular weight (M_w) had reduced to half of the original M_w.

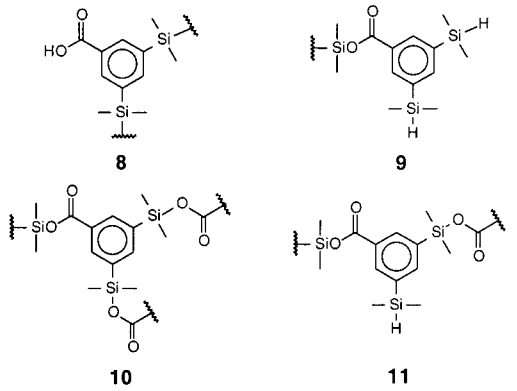


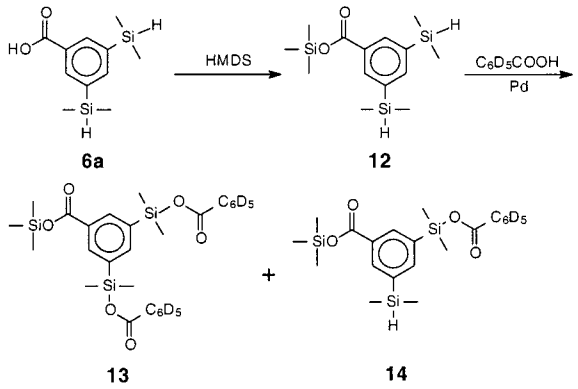
Figure 3. Repeat unit structures comprising the hyperbranched polymer **6b**.

original intensity upon polymerization, indicating 50% conversion of the dimethylhydrosilanes into the silyl ester functionalities. The relative chain propagation rates for the polymerizations decreased with increased steric bulk, in which the bulky isopropyl-substituted monomer, **5a**, required longer polymerization time than those of the methyl-substituted monomers **4a** and **6a**. Even though extreme efforts, including varying reaction temperature, catalyst, and solvent system, were taken in the attempts to obtain hyperbranched poly(diisopropylsilyl benzoate) **7b**, no occurrence of dehydrocoupling was detected between the carboxylic acid and the diisopropylsilyl group of **7a**.

Poly(silyl ester)s synthesized through dehydrocoupling chemistries were then isolated by evaporation of the solvent and characterized by infrared (IR), ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR INEPT spectroscopies, SEC, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) (Table 2). Because of the chain rigidity resulting from the high density of aromatic rings along the polymer backbone, each of the poly(silyl ester)s exhibited a glass transition (T_g) well above room temperature. The thermal stabilities of the poly(silyl ester)s were evaluated by TGA from 25 to 500 °C in N_2. Each of the three polymers exhibited no mass loss up to 350 °C.

Analysis of the structure[59] of hyperbranched molecule **6b** reveals that four different types of units are present, as shown in Figure 3. These include the single unit at the focal point **8**, the terminal repeat units **9**, which bear two hydrosilyl groups, the dendritic repeat units **10**, which bear no free hydrosilyl groups and two benzoyloxysilyl groups, and the linear repeat units **11**, which bear one hydrosilyl and one benzoyloxysilyl group. Of these, the presence of **8** can be ignored for the type of high molecular weight polymer we have obtained. The dendritic and terminal repeat units contribute to a branched structure, and the degree of branching (DB)

Scheme 3



is defined as the sum of dendritic and terminal units divided by the total sum of dendritic, terminal, and linear repeat units.[36−38,59] Determination of the relative numbers of each type of repeating unit was made by ^{1}H NMR analysis. To analyze the different proton resonances resulting from different aromatic ring substitutions in **6b**, three model compounds were prepared (Scheme 3). The reaction of **6a** with HMDS afforded the silyl ester **12**. Cross-dehydrocoupling between **12** and 2 equiv of benzoic acid in the presence of Pd catalyst gave entirely **13**, while the reaction of **12** with 1 equiv of benzoic acid gave a mixture of **13** and **14**. Benzoic-d_5 acid was used in this study in order to avoid complications in the interpretation of ^{1}H NMR from phenyl proton resonances. Compounds **12**, **13**, and **14** served as models for the terminal unit **9**, dendritic unit **10**, and linear unit **11**, respectively. Comparison of the ^{1}H NMR spectra (Figure 4) for **12**, **13**, and **14** revealed that unique proton resonances could be identified: the C-4 proton of **12** resonates at 7.89 ppm; the resonances of C-2 and C-6 protons of **13** are located at 8.46 ppm; the C-4 proton of **14** is observed at 8.07 ppm. The other aromatic resonances for model compounds **12**, **13**, and **14** are in the region of 8.22−8.36 ppm. Examination of the ^{1}H NMR spectrum of hyperbranched polymer **6b** revealed good correlation between the C-4 proton of **12** and the broad resonance observed at 7.85−7.95 ppm. Similarly, the broad set of resonances at 8.45−8.60 ppm was observed, corresponding to the C-2 and C-6 protons of **13**. The resonances at the region 8.05−8.20 ppm were correlated to the C-4 proton of **14**. Assigning these resonances to the corresponding protons in each repeat unit, followed by integration of each region, then allowed the relative percentage of terminal unit **9**, dentritic unit **10**, and linear unit **11** to be determined as 31%, 19%, and 49%, respectively. The DB for **6b** was then calculated to be 51%.

The degradation studies by hydrolysis were initially performed upon the poly(silyl ester)s as solutions in THF exposed to the laboratory environment (ca. 25 °C and 35% humidity), so that the inherent stability of the polymers could be evaluated without interferences from physical effects. The decreasing molecular weights of the polymers over time were observed through SEC analysis (Figure 5 and Figure 7), and the results have been converted to half-lives listed in Table 2. As previously reported,[23,24,26] the steric bulkiness of substituents attached to the silicon atoms greatly affected the relative degradation rates. The methyl-substituted poly(silyl ester)s **4b** and **6b** were substantially less stable toward nucleophilic attack than was the isopropyl-substituted polymer **5b**. Exposed to atmospheric water, **4b** and **6b**

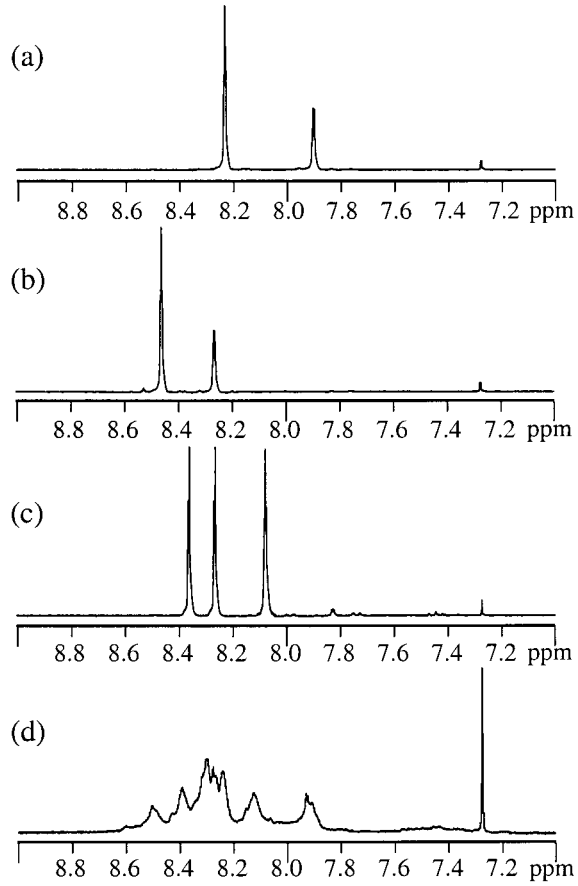


Figure 4. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of (a) **12**, (b) **13**, (c) **14**, and (d) **6b**. The resonance at 7.27 ppm is due to the presence of $CHCl_3$ in NMR solvent.

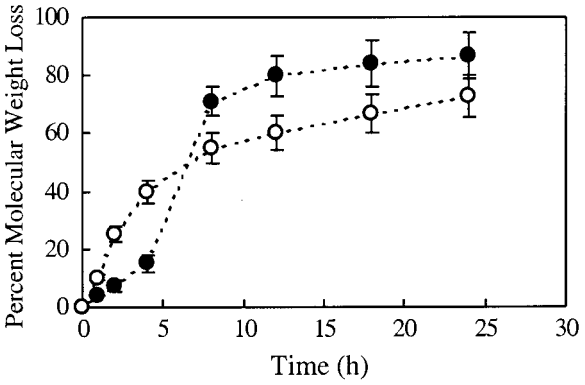


Figure 5. Plot of percent molecular weight loss vs time for linear and hyperbranched poly(dimethylsilyl ester)s in THF exposed to the laboratory environment (ca. 25 °C and 35% humidity): ○, **4b**; ●, **6b**. Values given are the average for the experiments repeated in triplicate, with the standard deviation as the error amount.

underwent 50% weight loss within 6 h, whereas **5b** exhibited a half-life of about 6 days. Hyperbranched poly(silyl ester) **6b** demonstrated an interesting degradation profile (Figure 5). Unlike the degradation behavior of linear poly(silyl ester)s prepared in our previous work,[22−26] which included a rapid initial degradation rate followed by ever-decreasing decomposition rate over the remainder of the degradation time scale, the hyperbranched polymer **6b** exhibited a slow initial molecular weight loss, followed by rapid hydrolytic cleavage. This phenomenon is expected to be an artifact of the SEC method by which the degradation

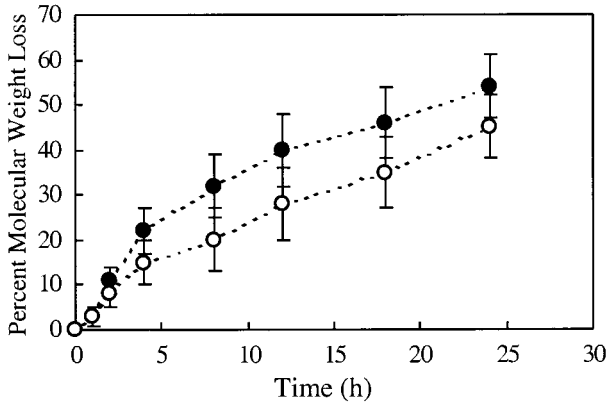


Figure 6. Plot of percent molecular weight loss vs time for linear and hyperbranched poly(dimethylsilyl ester)s as bulk samples exposed to the laboratory environment (ca. 25 °C and 35% humidity): ○, **4b**; ●, **6b**. Values given are the average for the experiments repeated in triplicate, with the standard deviation as the error amount.

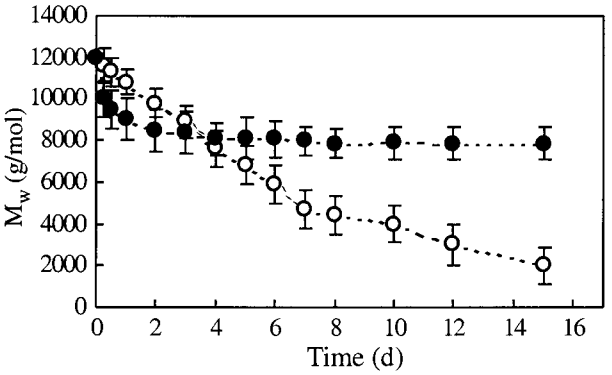


Figure 7. Plot of M_w vs time for **5b** exposed to the laboratory environment (ca. 25 °C and 35% humidity): ○, in THF; ●, as bulk sample. Values given are the average for the experiments repeated in triplicate, with the standard deviation as the error amount.

was monitored as molecular weight loss, rather than a difference in degradation rates. These findings support the original hypothesis of the different degradation behaviors for hyperbranched vs linear polymers. As the cleavage of the linear polymer chains occurred in random fashion to rapidly break down the molecular weight, similar random hydrolysis of the silyl ester linkages in the hyperbranched structure reduced the molecular weight in smaller increments, because 31% of the silyl ester linkages, as determined by NMR experiments with the help of model compounds, are present as chain ends (Figure 8). No molecular weight loss would be observed for cleavage of a bond that is part of a macrocyclic unit. The possibility of macrocycle formation has been discussed in several reports of hyperbranched polymerizations.[60−62]

Degradation studies of the poly(silyl ester)s as neat samples exposed to the laboratory environment (ca. 25 °C and 35% humidity) were then performed (Figures 6 and 7). The degradations of these poly(silyl ester)s in their solid states were all slower than those observed for the hydrolysis of the polymers in solution. For example, in THF solution, the molecular weight of **4b** and **6b** decreased rapidly within a few hours; however, samples stored in bulk exhibited only a slight decrease in molecular weight within the same time period and demonstrated a half-life of ca. 1 day for both **4b** and **6b**. For **5b**, after an initial drop in molecular weight,

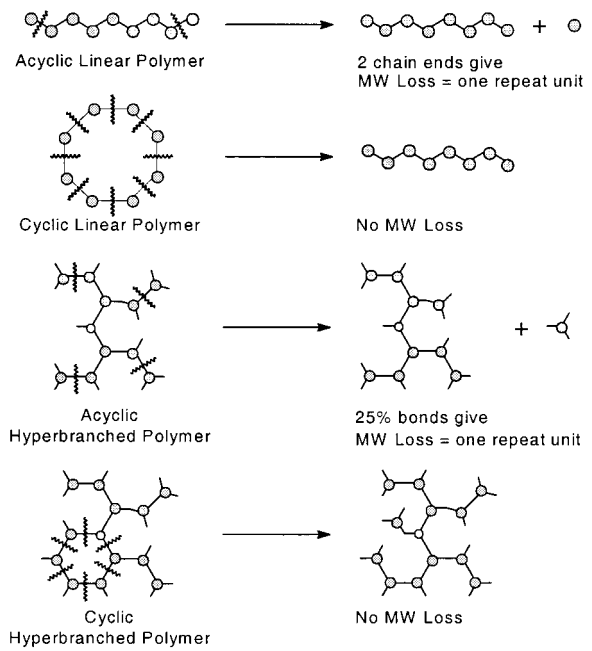


Figure 8. Schematic diagrams describing the architectural effect upon the change of molecular weight at the initial stage of polymer degradation.

the polymer exhibited good stability for long times in the solid state.

The polymer degradation was further evaluated topographically by analysis of the erosion processes[18] using AFM[48−51] (Figure 9). Polymer films were prepared by spin-casting THF solutions onto mica substrates and then allowed to remain exposed to the atmospheric water while being monitored by AFM. The AFM images in Figure 9 are representative of the topographies recorded before and during the erosion process. When the surface of the polymer film was exposed to atmospheric water, degradation of the polymer was initiated and led to an increased prominence of a granular surface. This interfacial change was quantified by the analysis of the root-mean-square (rms) surface roughness of the images (Figure 10). For noncrystalline polymer samples, two factors here controlled the erosion taking place: bond stability and hydrophobicity of the polymeric materials. Polymer **5b** exhibited little or no observable change over the recording time of 10 days, which agreed well with its enhanced hydrolytic stability as bulk samples in the solid state (Figure 7). In contrast, for the degradation of **6b**, an increase in the prominence of granules evenly distributed over the surface was observed in the AFM images. As the hydrolytic degradation continued, the rms values increased from 0.7 to 2.5 nm within the first 4 days; then, as the granules collapsed, leading to decreased height and increased diameter of the particles, the rms reduced to 1.5 nm over the remainder of the degradation time scale. At the

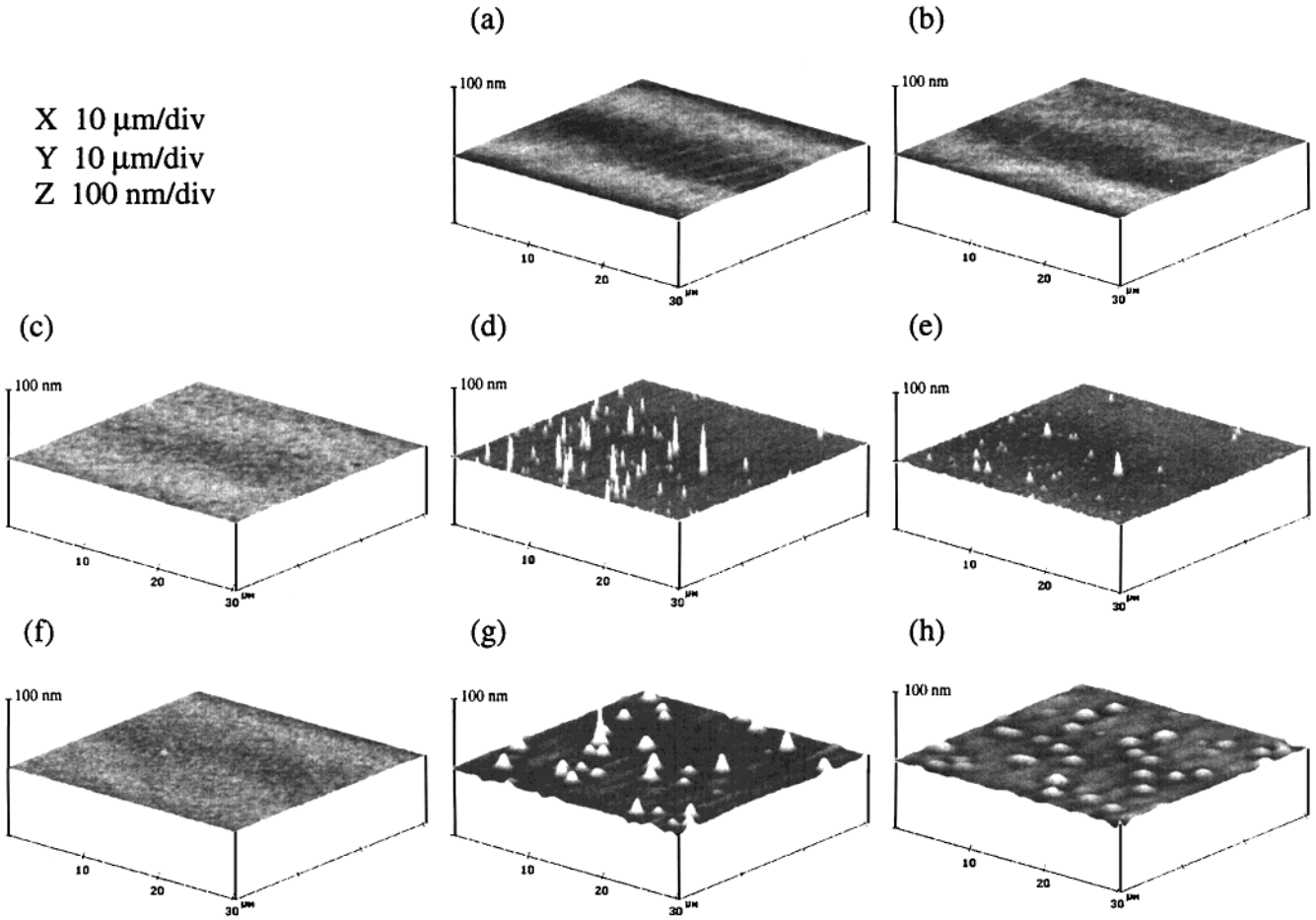


Figure 9. 30 μm × 30 μm AFM images of poly(silyl ester) thin films eroding upon the exposure to the laboratory environment (ca. 25 °C and 35% humidity): (a) **5b** (neat) at 0 min; (b) **5b** (neat) at 7 days; (c) **6b** (neat) at 0 min; (d) **6b** (neat) at 4 days; (e) **6b** (neat) at 10 days; (f) **6b** (containing 5 wt % ethyl glycol diethyl ether) at 0 min; (g) **6b** (containing 5 wt % ethylene glycol diethyl ether) at 2 days; (h) **6b** (containing 5 wt % ethyl glycol diethyl ether) at 10 days. The images taken at time 0 min were recorded in a N_2 atmosphere.

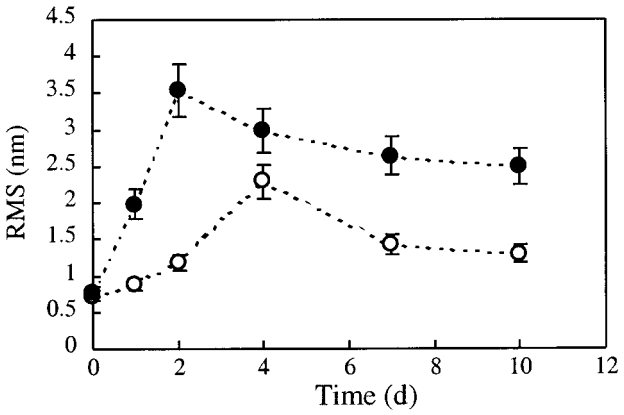


Figure 10. Root-mean-square surface roughness (rms) of the area shown in Figure 9: ○, **6b** neat; ●, **6b** containing 5 wt % ethylene glycol diethyl ether. Values given are the average for the experiments repeated in triplicate, with the standard deviation as the error amount.

degradation time of 10 days, the granules had diameters between 0.5 and 2 μm and heights between 5 and 40 nm. To evaluate the effect of hydrophobicity/hydrophilicity of materials upon the erosion process, a film sample of the polymer containing a high boiling point hygroscopic solvent, ethylene glycol diethyl ether, was prepared. It was found that the presence of the hygroscopic solvent promoted the penetration of moisture, thereby increasing the degradation rate, as observed by the formation of granules of larger size and increased surface roughness in a shorter period of time. As the erosion process was monitored for sample **6b**, containing 5 wt % of ethylene glycol diethyl ether, the rms value increased from 0.7 to 3.6 nm within the first 2 days and then decreased to 2.5 nm over the remainder of the degradation time scale. At 10 days, the granules had diameters between 2 and 5 μm and heights between 5 and 30 nm.

Conclusions

AB_n-type polymerizations (where $n = 1$ or 2) based upon cross-dehydrocoupling reactions for the preparation of poly(silyl ester)s with differing compositions and architectures were designed to obtain polymers with various hydrolytic stabilities and degradation profiles. The cross-dehydrocoupling chemistry provided a route whereby sterically bulky isopropyl substituents could be incorporated into the AB monomer-based polymerization to generate hydrolytically stabilized poly(silyl ester)s. Erosion processes of the bulk polymer samples were studied using AFM to enable visualization of the effects of degradation processes upon the dynamic topographical profile. The unique degradative profile observed for the hyperbranched poly(silyl ester)s is of great interest, and further modification of the degradation properties is being accomplished by compositional and architectural control for the poly(silyl ester)s.

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. IR spectra were obtained on a Perkin-Elmer Spectrum BX FT-IR system using the diffuse reflectance method. The samples were powdered or cast from solution and loaded on abrasive sampling sticks. KBr was used as nonabsorbing standard to give the background spectrum. ^{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 on a Varian Unity-plus spectrometer at 75 MHz with the solvent carbon signal as standard. ^{29}Si NMR spectra were recorded using standard INEPT[63] (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. 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 Corporation, Houston, TX). Two 5 μm Polymer Laboratories PL_{gel} columns (300 × 7.7 mm) connected in series in order of increasing pore size 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 (T_g's) 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 200 °C. T_g was taken as the midpoint of the inflection tangent. Thermogravimetric analyses were performed in N_2 atmosphere on a Perkin-Elmer TGS-2 thermogravimetric analyzer. Heating rates were 10 °C/min up to 500 °C. For both DSC and TGA, the Perkin-Elmer instruments were upgraded with Instrument Specialists, Inc. (Antioch, IL), temperature program interface-PE, and the data were acquired and analyzed using TA-PC software version 2.11a (Instrument Specialists, Inc.).

Atomic force microscopy studies of morphologies of eroding polymer films were carried out with the aid of a Multimode Nanoscope IIIa system (Digital Instruments, Santa Barbara, CA), equipped with the J-type vertical engage scanner. Contact mode experiments were performed with standard, 100 μm long, wide-leg Si_3N_4 cantilevers (nominal spring constant 0.32 N/m). Freshly cleaved mica (New York Mica Co.) was used as the substrate for ultrathin films, which were spin-coated by directly depositing a 20 μL drop of polymer solutions in THF (typical concentration 10 mg/mL) at the surface of substrates rotating at 3500 rpm for 10 min. The film thicknesses were measured with AFM by measuring the depths of 1 μm × 1 μm holes machined with the probe operating at high contact force and were in the range 25−35 nm. Images taken at 0 min were recorded under an atmosphere of N_2 to minimize the role of humidity. Removal of N_2 protection and exposure to atmospheric water initiated further erosion processes.

Materials. Tetrahydrofuran (THF) (Omnisolv grade) was purchased from EM Science and distilled from sodium/benzophenone. Ethylene glycol diethyl ether and toluene were purchased from Aldrich and distilled from sodium. *N*,*N*-Dimethylformamide (DMF) was purchased from Aldrich and distilled under reduced pressure from CaO. Silicon compounds were purchased from United Chemical Technologies and distilled immediately prior to use. Benzoic-d_5 acid was purchased from Cambridge Isotope Laboratories, Inc. All other chemicals were purchased from Aldrich and used as received.

Methyl 4-(Diisopropylsilyl)benzoate (3). A solution of methyl 4-iodobenzoate (6.99 g, 0.0267 mol) in THF (30 mL) was cooled to −40 °C, and isopropylmagnesium chloride in THF (14 mL, 0.027 mol; 2.0 M) was added dropwise through an addition funnel. After 2 h at −40 °C, chlorodiisopropylsilane (4.02 g, 0.0267 mol) was added. After stirring for 12 h, the reaction mixture was worked up with dilute acid, and the products were extracted into diethyl ether. Removal of volatile solvents gave a crude yellow oil, which was purified by distillation using a Büchi Kugelrohr apparatus (ca. 125 °C, 0.2 mmHg) to give a colorless liquid (5.68 g, 0.0227 mol): yield 85%. IR: 3025, 2945, 2893, 2864, 2103, 1728, 1280, 1189, 883, 820, 802 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.01 (d, $J = 7$ Hz, 6H, $-CH(CH_3)_2$), 1.10 (d, $J = 7$ Hz, 6H, $-CH(CH_3)_2$), 1.28 (m, 2H, $-CH(CH_3)_2$), 3.94 (s, 3H, $-OCH_3$), 3.99 (t, $J = 3$ Hz, 1H, $-Si(C_3H_7)_2H$), 7.61 (d, $J = 8$ Hz, 2H, ArH), 8.01 (d, $J = 8$ Hz, 2H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.52 ($-CH(CH_3)_2$), 18.34 ($-CH(CH_3)_2$), 18.52 ($-CH(CH_3)_2$), 52.05 ($-OCH_3$), 128.34 (ArC), 130.60 (ipso ArC), 135.41 (ArC), 140.73 (ipso ArC), 167.26 (carbonylC) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 6.0 ppm. HR-MS: MH^+, 251.1467; calcd, 251.1467 for

$C_{14}H_{22}O_2Si$ (250.14). Elemental analysis: C, 66.92%; H, 8.71%. Calcd: C, 67.15%; H, 8.86%.

General Procedure for the Synthesis of Monomers. A solution of 1,4-dibromobenzene (for **4a** and **5a**) or 1,3,5-tribromobenzene (for **6a** and **7a**) in THF (ca. 1 M) was added dropwise to magnesium under Ar with stirring and heated at reflux for 24 h. A solution of chlorodialkylsilane in THF (ca. 2 M) was then added dropwise, and heating was continued with stirring for another 24 h. The reaction was cooled to −5 °C, and CO_2 was bubbled into the reaction through a gas dispersion tube for 2 h. The mixture was worked up with dilute acid, and the products were extracted into diethyl ether. The solvents were removed in vacuo, and the viscous oil was purified using silica gel flash column chromatography (CH_2Cl_2/diethyl ether gradient as the eluent; the concentrations were 0, 5, 10, and 20 vol % of diethyl ether). The product was further purified by recrystallization or distillation using a Büchi Kugelrohr apparatus.

4-(Dimethylsilyl)benzoic Acid (4a). This was prepared from 1,4-dibromobenzene (30.00 g, 0.1272 mol), magnesium (6.18 g, 0.254 mol), and chlorodimethylsilane (12.04 g, 0.1272 mol) and purified by recrystallization in diethyl ether (7.80 g, 0.0432 mol): yield 34%. IR: 3300−2500, 2122, 1698, 1304, 1255, 931, 909, 842, 815 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.40 (d, J = 3 Hz, 6H, $-Si(CH_3)_2H$), 4.48 (septet, J = 3 Hz, 1H, $-Si(CH_3)_2H$), 7.68 (d, J = 8 Hz, 2H, Ar**H**), 8.10 (d, J = 8 Hz, 2H, Ar**H**) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ −4.04 ($-Si(CH_3)_2H$), 129.15 (Ar**C**), 129.72 (ipso Ar**C**), 134.10 (Ar**C**), 145.04 (ipso Ar**C**), 171.98 (carbonyl**C**) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ −16.3 ppm. HR-MS: MH^+, 181.0684; calcd, 181.0685 for $C_9H_{12}O_2Si$ (180.06). Elemental analysis: C, 60.18%; H, 6.59%. Calcd: C, 59.96%; H, 6.71%.

4-(Diisopropylsilyl)benzoic Acid (5a). This was prepared from 1,4-dibromobenzene (20.47 g, 0.08677 mol), magnesium (4.22 g, 0.174 mol), and chlorodiisopropylsilane (13.08 g, 0.08677 mol) and purified by distillation (ca. 150 °C, 0.2 mmHg) as a white solid (7.80 g, 0.0330 mol): yield 38%. IR: 3300−2500, 2101, 1700, 1302, 1188, 882, 852, 816 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.02 (d, J = 7 Hz, 6H, $-CH(CH_3)_2$), 1.10 (d, J = 7 Hz, 6H, $-CH(CH_3)_2$), 1.29 (m, 2H, $-CH(CH_3)_2$), 4.02 (t, J = 3 Hz, 1H, $-Si(C_3H_7)_2H$), 7.66 (d, J = 8 Hz, 2H, Ar**H**), 8.11 (d, J = 8 Hz, 2H, Ar**H**) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.55 ($-CH(CH_3)_2$), 18.38 ($-CH(CH_3)_2$), 18.55 ($-CH(CH_3)_2$), 128.93 (Ar**C**), 129.76 (ipso Ar**C**), 135.53 (Ar**C**), 142.08 (ipso Ar**C**), 172.55 (carbonyl**C**) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 6.1 ppm. HR-MS: MH^+, 237.1304; calcd, 237.1311 for $C_{13}H_{20}O_2Si$ (236.12). Elemental analysis: C, 66.07%; H, 8.45%. Calcd: C, 66.05%; H, 8.53%.

3,5-Bis(dimethylsilyl)benzoic Acid (6a). This was prepared from 1,3,5-tribromobenzene (8.00 g, 0.0254 mol), magnesium (1.85 g, 0.0762 mol), and chlorodimethylsilane (4.81 g, 0.0508 mol) and purified by distillation (ca. 100 °C, 0.01 mmHg) as a white solid (1.03 g, 0.00432 mol): yield 17%. IR: 3300−2500, 2134, 1701, 1325, 1252, 1100, 950, 897, 709 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.40 (d, J = 3 Hz, 12H, $-Si(CH_3)_2H$), 4.50 (septet, J = 3 Hz, 2H, $-Si(CH_3)_2H$), 7.95 (t, J = 2 Hz, 1H, Ar**H**), 8.30 (d, J = 2 Hz, 2H, Ar**H**) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ −3.86 ($-Si(CH_3)_2H$), 127.91 (ipso Ar**C**), 136.44 (ipso Ar**C**), 137.52 (Ar**C**), 145.02 (Ar**C**), 172.78 (carbonyl**C**) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ −16.3 ppm. HR-MS: MH^+, 239.0918; calcd, 239.0924 for $C_{11}H_{18}O_2Si_2$ (238.08). Elemental analysis: C, 55.34%; H, 7.78%. Calcd: C, 55.41%; H, 7.61%.

3,5-Bis(diisopropylsilyl)benzoic Acid (7a). This was prepared from 1,3,5-tribromobenzene (17.41 g, 0.05530 mol), magnesium (4.03 g, 0.166 mol), and chlorodiisopropylsilane (16.67 g, 0.1106 mol) and purified by distillation (ca. 200 °C, 0.01 mmHg) as a white solid (4.07 g, 0.0116 mol): yield 21%. IR: 3300−2500, 2109, 1696, 1298, 1165, 919, 882, 822, 706 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.00 (d, J = 7 Hz, 12H, $-CH(CH_3)_2$), 1.09 (d, J = 7 Hz, 12H, $-CH(CH_3)_2$), 1.25 (m, 4H, $-CH(CH_3)_2$), 3.96 (t, J = 3 Hz, 2H, $-Si(C_3H_7)_2H$), 7.88 (t, J = 2 Hz, 1H, Ar**H**), 8.28 (d, J = 2 Hz, 2H, Ar**H**) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.55 ($-CH(CH_3)_2$), 18.38 ($-CH(CH_3)_2$), 18.57 ($-CH(CH_3)_2$), 127.57 (ipso Ar**C**), 133.96 (ipso Ar**C**), 137.71 (Ar**C**), 147.77 (Ar**C**), 172.10 (carbonyl**C**) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 5.9 ppm. HR-MS: MH^+, 351.2161; calcd 351.2175 for $C_{19}H_{34}O_2Si_2$ (350.21). Elemental analysis: C, 65.33%; H, 9.56%. Calcd: C, 65.08%; H, 9.77%.

General Procedure for the Synthesis of Poly(silyl ester)s. To a 10 mL Schlenk flask was added monomer in ethylene glycol diethyl ether to form a 10 M solution of reagents, followed by 0.25 mol % of 10 wt % Pd/C as the catalyst. After the rapid evolution of hydrogen had nearly ceased (about 30 min), the temperature was raised to 100 °C and maintained for 1−3 days under Ar. Because of the hydrolytic instabilities of the polymers, purification involved only evacuation (0.2 mmHg) of the reaction flask at 50 °C for 6 h to remove any remaining ethylene glycol diethyl ether. However, removal of the catalyst via filtration was done prior to SEC analysis and solvent-casting for AFM characterization.

Poly(dimethylsilyl benzoate) (4b). This was prepared from **4a** for 1 day. T_g = 75 °C. IR: 3063, 3026, 2959, 2893, 2819, 1690, 1298, 1255, 1096, 824 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.71 (s, 6H, $-Si(CH_3)_2-$), 7.80 (d, J = 8 Hz, 2H, Ar**H**), 8.09 (d, J = 8 Hz, 2H, Ar**H**) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ −1.61 ($-Si(CH_3)_2-$), 129.40 (Ar**C**), 132.21 (ipso Ar**C**), 133.55 (Ar**C**), 141.94 (ipso Ar**C**), 166.44 (carbonyl**C**) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 13.3 ppm. M_w = 3000 g/mol; M_w/M_n = 1.5, based upon SEC with polystyrene standards.

Poly(diisopropylsilyl benzoate) (5b). This was prepared from **5a** for 3 days. T_g = 89 °C. IR: 3070, 3030, 2948, 2863, 1698, 1292, 1187, 1095, 757, 698 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.12 (d, J = 7 Hz, 6H, $-CH(CH_3)_2$), 1.18 (d, J = 7 Hz, 6H, $-CH(CH_3)_2$), 1.68 (septet, 2H, $-CH(CH_3)_2$), 7.81 (d, J = 8 Hz, 2H, Ar**H**), 8.18 (d, J = 8 Hz, 2H, Ar**H**) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.48 ($-CH(CH_3)_2$), 17.42 ($-CH(CH_3)_2$), 129.52 (Ar**C**), 132.20 (ipso Ar**C**), 134.78 (Ar**C**), 139.50 (ipso Ar**C**), 166.44 (carbonyl**C**) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 13.6 ppm. M_w = 12 000 g/mol; M_w/M_n = 2.3, based upon SEC with polystyrene standards.

Hyperbranched Poly(dimethylsilyl benzoate) (6b). This was prepared from **6a** for 1 day. T_g = 41 °C. IR: 3020, 2893, 2819, 2125, 1705, 1302, 1266, 1086, 902, 853, 806, 699 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.40 (m, 50% 6H, $-Si(CH_3)_2H$), 0.75 (m, 50% 6H, $-Si(CH_3)_2O-$), 4.50 (m, 50% 1H, $-Si(CH_3)_2H$), 7.70−8.60 (br m, 3H, Ar**H**) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ −3.86 ($-Si(CH_3)_2H$), −1.41 ($-Si(CH_3)_2O-$), 127.80−137.50 (Ar**C**), 168.99 (carbonyl**C**) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ −16.3, 13.2 ppm. M_w = 23 000 g/mol; M_w/M_n = 6.8, based upon SEC with polystyrene standards.

Trimethylsilyl 3,5-Bis(dimethylsilyl)benzoate (12). To a solution of **6a** (0.77 g, 3.2 mmol) in THF (5 mL) was added slowly by syringe 1,1,1,3,3,3-hexamethyldisilazane (HMDS) (0.68 mL, 3.2 mmol) with stirring under Ar. The reaction was heated at reflux for 4 h. The solvent and excess HMDS were removed under reduced pressure, and the product was purified by distillation using a Büchi Kugelrohr apparatus (ca. 75 °C, 0.01 mmHg) as a colorless liquid (0.86 g, 2.8 mmol): yield 87%. ^1H NMR (300 MHz, $CDCl_3$): δ 0.42 (d, J = 3 Hz, 12H, $-Si(CH_3)_2H$), 0.46 (s, 9H, $-Si(CH_3)_3$), 4.52 (septet, J = 3 Hz, 2H, $-Si(CH_3)_2H$), 7.89 (t, J = 2 Hz, 1H, Ar**H**), 8.23 (d, J = 2 Hz, 2H, Ar**H**) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ −3.84 ($-Si(CH_3)_2H$), −0.16 ($-Si(CH_3)_3$), 129.79 (ipso Ar**C**), 136.39 (ipso Ar**C**), 137.13 (Ar**C**), 144.09 (Ar**C**), 167.10 (carbonyl**C**) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ −16.3 ($ArSi(CH_3)_2H$), 25.0 ($ArCOOSi(CH_3)_3$) ppm.

Trimethylsilyl 3,5-Bis(benzoyloxydimethylsilyl)benzoate (13). To a solution of **12** (0.30 g, 0.97 mmol) and benzoic-d_5 acid (0.49 g, 3.9 mmol) in THF (1 mL) was added 0.25 mol % of 10 wt % Pd/C as the catalyst with stirring under Ar. After the rapid evolution of hydrogen had nearly ceased (about 30 min), the reaction was heated at reflux for 24 h. The solvent was removed under reduced pressure. ^1H NMR (300 MHz, $CDCl_3$): δ 0.36 (s, 9H, $-Si(CH_3)_3$), 0.67 (s, 12H, $-Si(CH_3)_2OCOC_6D_5$), 8.26 (t, J = 2 Hz, 1H, Ar**H**), 8.46 (d, J = 2 Hz, 2H, Ar**H**) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 13.1 ($ArSi(CH_3)_2OCOC_6D_5$), 24.8 ($ArCOOSi(CH_3)_3$) ppm.

Trimethylsilyl 3-Benzoyloxydimethylsilyl-5-(dimethylsilyl)benzoate (14). To solution of **12** (0.30 g, 0.97 mmol)

and benzoic-d_5 acid (0.12 g, 0.97 mmol) in THF (1 mL) was added 0.25 mol % of 10 wt % Pd/C as the catalyst with stirring under Ar. After the rapid evolution of hydrogen had nearly ceased (about 30 min), the reaction was heated at reflux for 24 h. The solvent was removed under reduced pressure, and the product was purified by distillation using a Büchi Kugelrohr apparatus (ca. 175 °C, 0.01 mmHg) as a colorless liquid (0.20 g, 0.46 mmol): yield 47%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.41 (s, 9H, $-Si(CH_3)_3$), 0.42 (d, $J = 3$ Hz, 6H, $-Si(CH_3)_2H$), 0.67 (s, 6H, $-Si(CH_3)_2OCOC_6D_5$), 4.52 (septet, $J = 3$ Hz, 1H, $-Si(CH_3)_2H$), 8.07 (t, $J = 2$ Hz, 1H, Ar*H*), 8.27 (t, $J = 2$ Hz, 1H, Ar*H*), 8.36 (t, $J = 2$ Hz, 1H, Ar*H*) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ −16.3 ($ArSi(CH_3)_2H$), 13.1 ($ArSi(CH_3)_2OCOC_6D_5$), 24.8 ($ArCOOSi(CH_3)_3$) ppm.

Degradation of Polymers in Solution. Approximately 10 mg of polymer was dissolved in 2 mL of THF. Exposure to the laboratory atmosphere (ca. 25 °C and 35% humidity) provided for degradation by water. At the appropriate times (0 min, 1 h, 2 h, 4 h, 8 h, 1 day, 2 days, 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. Samples of ca. 10 mg each of the polymer were placed into individual glass vials. The vials were open to the laboratory environment (ca. 25 °C and 35% humidity). At the appropriate times (0 min, 1 h, 2 h, 4 h, 8 h, 1 day, 2 days, etc.), the polymer samples were dissolved in THF, and the SEC chromatograms were obtained.

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