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Synthesis of Poly(silylenemethylenes) through Reactions Carried Out on Preformed Polymers. 2. Investigation of the Hydrosilation Route to Substituted Poly(silylenemethylenes)

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ABSTRACT: A series of polymers of the type $[Si(CH_3)(C_3H_6R)CH_2]_n$ where R = C_3H_7, NEt_2, carbazole, and $OC_2H_4OC_2H_4OCH_3$ were prepared by hydrosilation of the appropriate terminal olefin with the $[Si(H)(CH_3)CH_2]_n$ (**1**) polymer using Karsted's catalyst. It was found that hydrosilation of these olefins with **1** proceeds with a relatively high (80−95%) conversion of the polymer SiH groups. NMR and DSC data on these polymers as well as their relative thermal and oxidative stabilities are reported. The phenol-substituted polymers, $[Si(CH_3)(C_3H_6C_6H_4OH)X]_n$ (**5**), where X = O (**5e**) or CH_2 (**5f**), were also prepared and their stability toward base hydrolysis was evaluated. It was found that the polycarbosilane **5f** shows superior hydrolytic stability relative to the polysiloxane **5e**.

Introduction

Poly(silylenemethylenes) (PSMs) (polymers which have the general formula $[Si(R_1)(R_2)CH_2]_n$) were first prepared in the mid-1960s by the ring-opening polymerization (ROP) of disilacyclobutanes.[1] These polymers can be viewed as a "hybrid" organic−inorganic type of polymer which bridge the all-carbon backbone polyolefins and such inorganic polymers as the polysilanes, -siloxanes, and -phosphazenes. The relatively short C−C bond distance (1.53 Å) of the polyolefins often leads to high chain torsional barriers and consequently high glass and/or melting temperatures. On the other hand, the high polarity of the N═P and Si−O bonds of the polyphosphazenes and polysiloxanes, respectively, can lead to poor chemical stability, particularly to hydrolysis reactions. The length (1.90 Å)[2] and chemical stability[3] of the Si−C bonds that make up the PSM backbone offer the possibility of preparing polymers that can potentially combine the chemical inertness of polyolefins with the chain flexibility of the polysiloxanes and polyphosphazenes.

Another major advantage of the "inorganic polymers" over the all-carbon backbone polyolefins is their synthetic flexibility, allowing substitution reactions on the polymer chain through reactive functionalities such as ECl and EH (E = Si or P). In this manner, numerous polyphosphazenes and polysiloxanes have been prepared by modifications of preformed polymers such as poly(dichlorophosphazene)[4] and poly(methylhydridosiloxane).[5] Until recently, this route has not been employed for the preparation of PSMs presumably, in part, because there were no convenient synthetic procedures for the preparation of high molecular weight PSMs having reactive functionalities.[6]

Practically all of the PSMs reported so far have been prepared starting from disilacyclobutanes by using platinum complexes as ROP catalysts. This reaction proceeds best for alkyl-substituted disilacyclobutanes, and up until a few years ago, the range of PSMs prepared by this route was effectively limited to those having only alkyl and aryl functionalities.[1,7]

Recently, we reported the preparation of a series of PSMs having one or two chloro or hydrido substituents on each backbone silicon atom.[8] We have also reported the results of our investigation into the use of poly[(chloromethylsilylene)methylene] as a starting material for the synthesis of various alkoxy-, alkyl-, and fluoro-substituted PSMs.[9] We now describe the results of our efforts to use poly[(hydridomethylsilylene)methylene] in hydrosilation reactions designed to attach a wide range of substituents onto the PSM backbone through Si−C bonds.

Hydrosilation has been widely used as a method of introducing various R groups onto polysiloxane chains through the platinum-catalyzed reaction of olefins with $[Si(H)(CH_3)O]_n$. Surfactant, liquid crystalline, and electroluminescent polysiloxanes have been prepared in this way.[10] Several reports have also appeared in the literature regarding the preparation of the polycarbosilanes of the type $[Si(CH_3)(R)C_6H_4]_n$ or $[Si(Ph)(R)C_3H_6]_n$ by means of hydrosilation starting from $[Si(CH_3)(H)C_6H_5]_n$ and $[Si(Ph)(H)C_3H_6]_n$; however, the scope of this method has not been investigated to a significant extent.[11] Moreover, it is clear that the poly(silylenemethylene) backbone can potentially provide a higher density of such substituents than these other polycarbosilanes.

Results and Discussion

Since poly[(hydridomethyl)siloxane] has been the starting material of choice for practically all the substituted polysiloxanes prepared by means of hydrosilation reactions,[5,10] we chose the structurally related poly[(hydridomethylsilylene)methylene] as the starting point for the current investigation. This has allowed us to compare the properties of the new PSMs with those of the corresponding polysiloxanes.

The various terminal olefins that were employed in this study (Scheme 1) were selected to illustrate the scope of the method and the wide range of potential functionality (i.e., hydrophobicity, aqueous (acid) solubility, luminescence, ion binding, etc.) that could be imparted to the PSM through this route. The analogous polysiloxanes were also prepared by using similar reaction conditions. Both parent polymers, poly[(hydridomethylsilylene)methylene] and poly[(hydridomethyl)siloxane], had similar molecular weight (M_w = 2000−2300).

Integration of the peaks due to the $CH_2CH_2CH_2R$ groups to the peaks of the $SiCH_3$ or $SiCH_2$ protons in

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Scheme 1

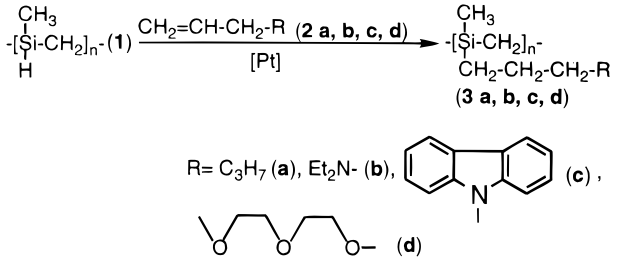


Table 1. Degree of Substitution (n) for the $[Si(CH_3)(C_3H_6R)X]_n[Si(CH_3)(H)X]_{1-n}$ Polymers

X	$R = C_3H_7$ (**3a**)	R = carbazole (**3c**)	$R = OC_2H_4OC_2H_4OCH_3$ (**3d**)
O	1.00	0.90	1.00
CH_2	0.95	0.80	0.90

the ^1H NMR spectra of the polymers indicates a typical degree of substitution of (Si)H by $(Si)CH_2CH_2CH_2R$ for the olefins studied of 80−95%, with a slightly higher degree of substitution, in general, for the corresponding polysiloxane (Table 1). For example, even after treatment of polymer **1** in refluxing 1-hexene in the presence of Karstedt's[12] catalyst for 24 h, the presence of residual SiH groups was still detectable by IR spectroscopy (the peak at 2100 cm^{-1}). In comparison, when poly[(hydridomethyl)siloxane] was hydrosilated under the same conditions, the SiH peak disappeared completely from the IR spectrum after 2 h of refluxing. These observations are consistent with the results of earlier studies[13] which have found that the rate of hydrosilation is retarded by electron-donating, and accelerated by electron-accepting, groups on the silicon. In this context, it is understandable that the less polar character of the SiC backbone in the PSMs, as compared to the polysiloxanes, causes the hydrosilation of **1** to proceed with greater difficulty than the hydrosilation of poly[(hydridomethyl)siloxane]. It also seems likely that the methylene groups in the backbone of **1** impose a higher steric barrier to reaction with the olefin than the oxygen atoms in the polysiloxane backbone.

Unlike the alkoxy-substituted poly[(methylsilylene)-methylenes],[9b] the ^{13}C NMR spectra of the hydrosilated PSMs did not show a clear splitting of the $SiCH_3$ and $SiCH_2Si$ peaks due to conformational effects (tacticity). Only the ^{13}C spectrum of the polymer **3a** shows a slight splitting of the $Si\mathit{C}H_2C_5H_{11}$ signal into three peaks (*rr*, *rm*=*mr*, *mr* triads) and the $Si\mathit{C}H_2Si$ signal into two peaks (*m* and *r* diads).[9b] The ^{29}Si NMR spectra of these polymers consists of a major peak at 2.3−2.6 ppm, due to the $[Si(Me)(C_3H_6R)CH_2]$ unit, along with, in some cases, a very minor peak at 16.5−17 ppm due to the $[Si(Me)(H)CH_2]$ unit. As expected,[13] all of the NMR spectra were consistent with α (anti-Markovnikov) addition of the olefins, with no sign of a β (Markovnikov) addition product in either the ^1H or ^{13}C NMR spectra.

As expected from the atactic structure of the starting polymer,[8a] all of the polymers prepared were amorphous. Their physical appearance ranged from viscous liquids (polymer **3d**) to solids (polymer **3c**). Compared to the corresponding polysiloxanes of similar molecular weight, the poly(silylenemethylene) polymers showed substantially higher T_g's (Table 2). This can again be attributed to the steric hindrance to chain torsion imposed by the hydrogens of the backbone methylene group.

Table 2. Physical Properties of the $[Si(Me)(C_3H_7R)X]_n$ Polymers

R	X	$M_n \times 10^3$	$M_w \times 10^3$	T_g (°C)
C_3H_7 (**3a**)	CH_2	3.2	18.1	−77.6
	O	3.3	12.2	−113.7
carbazole (**3c**)	CH_2	6.1	19.3	71.2
	O	5.8	17.8	59.9 (lit.[14] 51 °C)
$-O(C_2H_5O)_2CH_3$ (**3d**)	CH_2	5.3	23.2	−73.3
	O	5.5	22.1	−90.1

Table 3. Thermal Stability of the $[Si(Me)(C_3H_6R)X]_n$ Polymers

R	X	$M_n \times 10^3$	$M_w \times 10^3$	5% decomp temp[a] (°C)	10% decomp temp[a] (°C)
$-O(C_2H_5O)_2CH_3$ (**3d**)	CH_2	5.3	23.2	352	362
	O	5.5	22.1	338	350
C_3H_7 (**3a**)	CH_2	3.2	18.1	349	380
	O	3.3	12.2	316	375
carbazole (**3c**)	CH_2	6.1	19.3	407	425
	O	5.8	17.8	433	442

[a] TGA was carried out under nitrogen with a heating rate of 10 °C/min.

Polymer **3b** did not show a response on the DRI detector used in the GPC measurements. After the concentration of the polymer was increased to 5 wt %, a strong peak at the end of the run overlapping with the solvent peak was detected. Absorption of the polymer onto the GPC column was suspected here.[15] Polymer **3b** has a T_g of −61.2 °C. This polymer does not dissolve in pH 7 water but dissolves in aqueous HCl. After removal of all of the volatiles in vacuum, a waxy solid, presumably the hydrochloride salt of polymer **3b**, was isolated. This solid is soluble in water, and its NMR spectrum in D_2O is essentially the same as that of the amine form in $CDCl_3$. It has a T_g of −2.3 °C and decomposes at 140−150 °C by TGA. Addition of a base to the aqueous solution of the hydrochloride salt reprecipitates the original polymer **3b**, as evidenced by NMR spectroscopy.

The thermal stability of the poly(silylenemethylene) polymers was also evaluated and compared to the thermal stability of the corresponding siloxanes with similar molecular weights (Table 3). The thermal stability of all of these polymers depends strongly on the nature of the side chain attached to the silicon. It might be expected that the substitution of the oxygen in the polymer backbone by a methylene group would cause a decrease in the thermal, and especially the oxidative, stability of the PSMs compared to the polysiloxanes; however, no such simple correlation was observed. It appears instead that when the side chain itself is relatively thermally unstable, as is suggested by the relatively low T_{dec} observed in both N_2 and in air for the respective polymers (i.e., with the diethylene glycol or *n*-hexyl side chains), the PSMs tend to be more stable than the corresponding polysiloxanes. On the other hand, for those cases where the side chain itself is relatively thermally stable and the polymer chain appears to provide the "weakest link" (i.e., the polymers with relatively high T_{dec}), the polysiloxane polymers tend to be more stable in N_2 and in air than the corresponding PSMs (Tables 3 and 4).

In order to provide a direct comparison between the poly(silylenemethylenes) and the polysiloxanes in terms of hydrolytic stability, polymers **4** and **5** were synthesized as shown in Scheme 2.

In both cases deprotection of the trimethylsiloxy group seems to be complete as judged by NMR spectroscopy.

Table 4. Oxidative Stability of the $[Si(Me)(C_3H_6R)CH_2]_n$ Polymers

R	X	5% decomp temp[a] (°C)	10% decomp temp[a] (°C)
$O(C_2H_5O)_2CH_3$ (**3d**)	CH_2	268	305
	O	235	290
C_3H_7 (**3a**)	CH_2	290	310
	O	270	315
carbazole (**3c**)	CH_2	334	364
	O	390	410

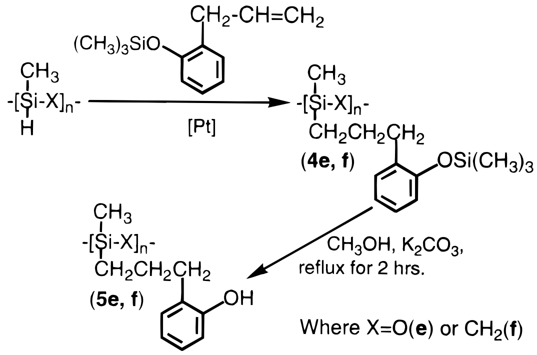
[a] TGA was performed in dry air at a heating rate of 10 °C/min.

Table 5. Hydrolytic Stability of a Substituted Poly(silylenemethylene) Compared to the Corresponding Polysiloxane

polymer	X = O	X = CH_2
M_w of **4** (TMS protected)	18200	19100
M_w of **5**/M_w of **5** calcd[a]	5200/13300	15900/13800
M_w of **5** after 24 h in 10% KOH at 25 °C	1500	15900
M_w of **5** after 120 h in 10% KOH at 25 °C		13000

[a] Assuming complete conversion of $C_6H_4OSi(CH_3)_3$ into C_6H_4OH.

Scheme 2



Polymers **5e,f** are soluble in basic aqueous solutions; their hydrolytic stability was evaluated in 10% aqueous KOH at 25 °C. The results are shown in Table 5.

As is evident from the table, the polysiloxane polymer starts to decompose even under the action of catalytic amounts of K_2CO_3 during the deprotection step. The poly(silylenemethylene) polymer in contrast does not show any significant reduction in its molecular weight until after 5 days of exposure to a 10% KOH solution. Its NMR spectrum also remains unchanged after recovery by HCl addition.

Conclusion

Despite the fact that the hydrosilation of poly[(hydridomethyl)methylene] polymer proceeds with somewhat greater difficulty than the hydrosilation of poly[(hydridomethyl)siloxane], we have found that hydrosilation is an effective and convenient method for the introduction of various side chains onto the poly(silylenemethylene) backbone with a high degree of substitution. Moreover, the resulting polymers have a thermal and oxidative stability that is comparable to the thermal stability of the corresponding polysiloxanes while affording a higher hydrolytic stability under strongly basic conditions.

Experimental Section

All manipulations involving air and/or moisture-sensitive materials were performed under N_2. All ether and hydrocarbon solvents were distilled before use from their purple sodium/benzophenone solutions. Allyldiethylamine (**2b**),[16a] *N*-allylcarbazole (**2d**),[16b] and poly[(hydridomethylsilylene)methylene][8a] were prepared according to the literature methods. Poly[hydridomethylsiloxane] ($M_w = 2200$) and chlorotrimethylsilane was purchased from Petrarch Systems Silanes & Silicones and used as such. Allylbromide, allylphenol, diethylene glycol methyl ether, and 1-hexene were purchased from Aldrich and dried over molecular sieves.

NMR spectra were obtained on XL-200 or Unity-500 instruments. ^1H and ^{13}C spectra were referenced to the solvent peaks, ^{29}Si spectra were referenced to TMS. GPC was carried out in THF solution, using a Waters 600 Multisolvent Delivery System with a differential refractometer detector and three Ultrastyragel columns in series; molecular weights are referenced to polystyrene standards. All DSC measurements were performed by using a heating rate of 10 °C/min on Sieko DSC 220C or TA 2920 instruments. The T_g was determined as the inflection point in the heating portion of the DSC curve, after an initial heating/cooling cycle. TGA measurements were performed on Perkin-Elmer TAC7 instrument with a heating rate of 10 °C/min under a flow of dry N_2 or dry air. Each run was repeated at least three times.

Preparation of Di(ethylene glycol)allyl Methyl Ether. Sodium (2.3 g, 0.1 mol) was gradually added to a solution of diethylene glycol methyl ether (12 g, 0.1 mol) in 70 mL of toluene. After refluxing the mixture for 6 h, it was cooled to 25 °C, 14.5 g (0.12 mol) of allyl bromide was added slowly, and the mixture was refluxed for another 2 h. After cooling, 20 mL of water was added slowly; the organic layer was separated, dried, and redistilled under reduced pressure. The fraction boiling at 40−45 °C (0.4 mmHg) was collected; yield, 8.5 g (52%, 98% purity by GC): 200 MHz ^1H NMR ($CDCl_3$) δ 5.75 (m, 1H, $CH_2{=}C\mathit{H}$), 5.18−5.00 (m, 2H, $C\mathit{H_2}{=}CH$), 3.88 (2H, $CH_2{=}CHC\mathit{H_2}O$), 3.59−3.34 (8H, $OC_2\mathit{H_4}O$), 3.24 (s, 3H, $OC\mathit{H_3}$); 50 MHz ^{13}C NMR ($CDCl_3$) δ 134.5 ($CH_2{=}\mathit{C}H$), 116.5 ($\mathit{C}H_2{=}CH$), 71.8, 71.6, 70.3, 70.2, 69.1 ($\mathit{C}H_2O(\mathit{C}_2H_4O)_2CH_3$), 58.6 ($\mathit{C}H_3O$)

Preparation of 1-(Trimethylsiloxy)-2-allylbenzene. 2-Allylphenol (10 g, 75 mmol) and triethylamine (7.5 g, 75 mmol) were dissolved in 60 mL of THF. To this solution, 15 g (140 mmol) of chlorotrimethylsilane was added slowly. The mixture was stirred for 3 h and the precipitated triethylamine hydrochloride was filtered off. The filtrate was redistilled at reduced pressure. The fraction boiling at 80−90 °C (0.4 mmHg) was collected; yield, 11 g (71%, 98% purity by GC): 200 MHz ^1H NMR ($CDCl_3$) δ 7.24−6.81 (4H, Ar), 6.00 (m, 1H, $CH_2{=}C\mathit{H}$), 5.10 (m, 2H, $C\mathit{H_2}{=}CH$), 3.39 (d, $J = 2.4$ Hz, 2H, $CH_2{=}CHC\mathit{H_2}$), 0.32 (s, 9H, $Si(C\mathit{H_3})_3$); 50 MHz ^{13}C NMR ($CDCl_3$) δ 153.2, 130.8, 130.1, 127.1, 121.3, 118.8 (Ar), 137.0 ($CH_2{=}\mathit{C}H$), 115.3 ($\mathit{C}H_2{=}CH$), 34.6 ($Ar\mathit{C}H_2$), 0.5 ($Si(\mathit{C}H_3)_3$).

Hydrosilation Procedure. To 10 mmol of poly[(hydridomethylsilylene)methylene], a 2-fold stoichiometric excess of olefin (olefin **2d** predissolved in a minimum amount of toluene) was added followed by 25−30 μL of 5% (wt [Pt]) solution of Karstedt's[12] catalyst in xylenes. The mixture was refluxed or maintained at 80 °C overnight. Then, in the case of polymers **3a,b,d**, the olefin was stripped off under vacuum; polymer **3c** and polymer **4e** were reprecipitated 3−5 times from a toluene/methanol mixture until olefin peaks could not be observed any longer in the 500 MHz ^1H NMR spectrum. The corresponding polysiloxanes were prepared in a similar manner.[17] For polymer **3a**: 500 MHz ^1H NMR ($CDCl_3$) δ 1.27 (br, $SiCH_2C_4\mathit{H_8}CH_3$), 0.88 (t, $J = 6.7$ Hz, $SiC_5H_{10}C\mathit{H_3}$), 0.50 (br, $SiC\mathit{H_2}C_5H_{11}$), 0.02 (s, $SiC\mathit{H_3}$), −0.28 (br, $SiC\mathit{H_2}Si$); 125 MHz ^{13}C NMR ($CDCl_3$) δ 33.63, 31.73, 24.23, 22.73 ($SiCH_2\mathit{C_4}H_8CH_3$), 19.15, 19.10, 19.05 ($Si\mathit{C}H_2C_5H_{11}$), 14.17 ($SiC_5H_{10}\mathit{C}H_3$), 3.59, 3.52 ($Si\mathit{C}H_2Si$), 0.94 ($Si\mathit{C}H_3$).

For polymer **3b**: 500 MHz ^1H NMR ($CDCl_3$) δ 2.42 (q, $J = 7.2$ Hz, $NC\mathit{H_2}CH_3$), 2.28 (t, $J = 7.4$ Hz, $SiC_2H_4C\mathit{H_2}NEt_2$), 1.31 (br, $SiCH_2C\mathit{H_2}$), 0.91 (t, $J = 6.7$ Hz, $NCH_2C\mathit{H_3}$), 0.33 (br, $SiC\mathit{H_2}C_2H_4NEt_2$), −0.06 (s, $SiC\mathit{H_3}$), −0.36 (br, $SiC\mathit{H_2}Si$); 125 MHz ^{13}C NMR ($CDCl_3$) δ 56.82 ($SiC_2H_4\mathit{C}H_2NEt_2$), 46.77 ($N\mathit{C}H_2CH_3$), 21.57 ($SiCH_2\mathit{C}H_2$), 16.41 ($CH_2\mathit{C}H_3$), 11.65 ($Si\mathit{C}H_2C_2H_4NEt_2$), 3.36 ($Si\mathit{C}H_2Si$), 0.75, 0.64 ($Si\mathit{C}H_3$). For **3b**·*m*HCl: 500 MHz ^1H NMR (D_2O) δ 2.88 (br, 4H, NCH_2CH_3), 2.76 (br, 2H,

$\mathrm{SiC_2H_4C}\mathit{H}_2\mathrm{NEt_2}$), 1.36 (br, 2H, $\mathrm{SiCH_2C}\mathit{H}_2$), 0.95 (br, $\mathrm{CH_2C}\mathit{H}_3$), 0.26 (br, 2H, $\mathrm{SiC}\mathit{H}_2\mathrm{C_2H_4NEt_2}$), −0.19 (s, 3H, $\mathrm{SiC}\mathit{H}_3$), −0.44 (br, 2H, $\mathrm{SiC}\mathit{H}_2\mathrm{Si}$).

For polymer **3c**: 500 MHz ^{1}H NMR ($\mathrm{C_6D_6}$) δ 7.96, 7.33, 7.15 (aryl), 3.73 (br, $\mathrm{SiC_2H_4C}\mathit{H}_2\mathrm{N}$), 1.45 (br, $\mathrm{SiCH_2C}\mathit{H}_2$), 0.2, −0.28, −0.68 ($\mathrm{SiC}\mathit{H}_2\mathrm{C_2H_4N}$, $\mathrm{SiC}\mathit{H}_3$, $\mathrm{SiC}\mathit{H}_2\mathrm{Si}$); 125 MHz ^{13}C NMR ($\mathrm{C_6D_6}$) δ 140.90, 125.95, 123.33, 120.88, 119.30, 109.07 (aryl), 45.56 ($\mathrm{SiC_2H_4}\mathit{C}\mathrm{H_2N}$), 23.77 ($\mathrm{SiCH_2}\mathit{C}\mathrm{H_2}$), 16.00 ($\mathrm{Si}\mathit{C}\mathrm{H_2C_2H_4N}$), 3.25 ($\mathrm{Si}\mathit{C}\mathrm{H_2Si}$), 0.62 ($\mathrm{Si}\mathit{C}\mathrm{H_3}$).

For polymer **3d**: 500 MHz ^{1}H NMR ($\mathrm{CDCl_3}$) δ 3.57, 3.53, 3.48 ($\mathrm{OC}\mathit{H}_2$), 3.30 (s, $\mathrm{OC}\mathit{H}_3$), 1.47 (br, $\mathrm{C}\mathit{H}_2\mathrm{CH_2Si}$), 0.38 (br, $\mathrm{OC_2H_5C}\mathit{H}_2\mathrm{Si}$), −0.04 ($\mathrm{SiC}\mathit{H}_3$), −0.35 ($\mathrm{SiC}\mathit{H}_2\mathrm{Si}$); 125 MHz ^{13}C NMR ($\mathrm{CDCl_3}$) δ 74.30, 71.77, 70.46, 70.35, 69.87 ($\mathrm{O}\mathit{C}\mathrm{H_2}$), 58.85 ($\mathrm{O}\mathit{C}\mathrm{H_3}$), 24.11 ($\mathrm{SiCH_2}\mathit{C}\mathrm{H_2}$), 14.34 ($\mathrm{Si}\mathit{C}\mathrm{H_2C_2H_5O}$), 3.14 ($\mathrm{Si}\mathit{C}\mathrm{H_2}$-Si), 0.59 ($\mathrm{Si}\mathit{C}\mathrm{H_3}$).

For polymer **4e**: 500 MHz ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.03, 6.81, 6.73 (aryl), 2.53 ($\mathrm{PhC}\mathit{H}_2$), 1.59 ($\mathrm{SiCH_2C}\mathit{H}_2$), 0.53 ($\mathrm{SiC}\mathit{H}_2\mathrm{CH_2}$), 0.24 $\{\mathrm{Si(C}\mathit{H}_3)_3\}$, 0.00 ($\mathrm{SiC}\mathit{H}_3$); 125 MHz ^{13}C NMR ($\mathrm{CDCl_3}$) δ 153.26, 133.08, 130.04, 126.46, 121.16, 118.61 (aryl), 33.92 ($\mathit{C}\mathrm{H_2Ph}$), 23.31 ($\mathrm{SiCH_2}\mathit{C}\mathrm{H_2}$), 17.77 ($\mathrm{Si}\mathit{C}\mathrm{H_2CH_2}$), 0.50 ($\mathrm{Si(}\mathit{C}\mathrm{H_3)_3}$), −0.33 ($\mathrm{Si}\mathit{C}\mathrm{H_3}$). 99 MHz ^{29}Si NMR ($\mathrm{CDCl_3}$) δ 18.15 ($\mathit{Si}\mathrm{(CH_3)_3}$), −22.64 ($\mathrm{O}\mathit{Si}\mathrm{O}$).

For polymer **4f**: 500 MHz ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.17, 7.11, 6.93, 6.84 (aryl), 2.65 ($\mathrm{C}\mathit{H}_2\mathrm{Ph}$), 1.62 ($\mathrm{SiCH_2C}\mathit{H}_2$), 0.65 ($\mathrm{SiC}\mathit{H}_2$-$\mathrm{CH_2}$), 0.33 $\{\mathrm{Si(C}\mathit{H}_3)_3\}$, 0.11 ($\mathrm{SiC}\mathit{H}_3$), −0.20 ($\mathrm{SiC}\mathit{H}_2\mathrm{Si}$); 125 MHz ^{13}C NMR ($\mathrm{CDCl_3}$) δ 153.23, 133.27, 130.15, 126.55, 121.16, 118.66 (aryl), 34.71 ($\mathit{C}\mathrm{H_2Ph}$), 24.76 ($\mathrm{SiCH_2}\mathit{C}\mathrm{H_2}$), 19.28 ($\mathrm{Si}\mathit{C}\mathrm{H_2}$), 3.44 ($\mathrm{Si}\mathit{C}\mathrm{H_2Si}$), 0.56 ($\mathrm{Si(}\mathit{C}\mathrm{H_3)_3}$), 0.25 ($\mathrm{Si}\mathit{C}\mathrm{H_3}$); 99 MHz ^{29}Si NMR ($\mathrm{CDCl_3}$) δ 18.23 ($\mathit{Si}\mathrm{(CH_3)_3}$), 2.09 ($\mathrm{CH_2}\mathit{Si}\mathrm{CH_2}$).

Preparation of Polymers 5e,f. Polymers **4e,f** (1 g) were suspended in 20 mL of methanol. A small amount (2−5 mg) of potassium carbonate was added, and the mixture was brought to reflux. After all the polymer had dissolved, refluxing was continued for another 5 h. Methanol was stripped off, and the residue was reprecipitated from a THF/hexane mixture. For polymer **5e**: 500 MHz ^{1}H NMR (acetone-d_6): δ 7.03, 6.94, 6.82, 6.70 (aryl), 4.8 (very br, $\mathrm{PhO}\mathit{H}$), 2.63 ($\mathrm{PhC}\mathit{H}_2$), 1.71 ($\mathrm{SiCH_2C}\mathit{H}_2$), 0.62 ($\mathrm{SiC}\mathit{H}_2\mathrm{CH_2}$), 0.06 ($\mathrm{SiC}\mathit{H}_3$); 125 MHz ^{13}C NMR (acetone-d_6) δ 156.01, 130.86, 129.55, 127.36, 119.95, 115.72 (aryl), 34.40 ($\mathit{C}\mathrm{H_2Ph}$), 24.18 ($\mathrm{SiCH_2}\mathit{C}\mathrm{H_2}$), 18.36 ($\mathrm{Si}\mathit{C}\mathrm{H_2CH_2}$), 0.14 ($\mathrm{Si}\mathit{C}\mathrm{H_3}$).

For polymer **5f**: 500 MHz ^{1}H NMR (acetone-d_6) δ 7.04 6.92, 6.88, 6.66 (aryl), 2.67 ($\mathrm{C}\mathit{H}_2\mathrm{Ph}$), 1.66 ($\mathrm{SiCH_2C}\mathit{H}_2$), 0.66 ($\mathrm{SiC}\mathit{H}_2$-$\mathrm{CH_2}$), 0.07 (3H, $\mathrm{SiC}\mathit{H}_3$), −0.17 ($\mathrm{SiC}\mathit{H}_2\mathrm{Si}$); 125 MHz ^{13}C NMR (acetone-d_6) δ 156.71, 130.72, 129.86, 127.29, 119.31, 116.15 (aryl), 35.18 ($\mathit{C}\mathrm{H_2Ph}$), 25.45 ($\mathrm{SiCH_2}\mathit{C}\mathrm{H_2}$), 19.76 ($\mathrm{Si}\mathit{C}\mathrm{H_2CH_2}$), 4.16 ($\mathrm{Si}\mathit{C}\mathrm{H_2Si}$), 1.48 ($\mathrm{Si}\mathit{C}\mathrm{H_3}$).

Test of Hydrolytic Stability of Polymers 5e,f. Polymers **5e,f** (0.5 g) were dissolved in 20 mL of 10% aqueous KOH. After the desired time period, the polymer was reprecipitated by neutralizing the solution with 4 M HCl. The solid product was dissolved in THF, the solution was filtered, and the THF was stripped off under vacuum. The obtained polymer was examined by GPC.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of polymers **3a−d** and **5f** (11 pages). Ordering information is given on any current masthead page.

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(17) For $[\mathrm{Si(Me)(C_3H_6\text{-}carbazole)\text{-}O}]_n$ 500 MHz ^{1}H NMR ($\mathrm{CDCl_3}$): δ 8.00, 7.12, 6.99 (aryl), 3.69 (br, $\mathrm{SiC_2H_4C}\mathit{H}_2\mathrm{N}$), 1.39 (br, $\mathrm{SiCH_2C}\mathit{H}_2$), 0.01 (br, $\mathrm{SiC}\mathit{H}_2\mathrm{C_2H_4N}$), −0.48 (s, $\mathrm{SiC}\mathit{H}_3$). 125 MHz ^{13}C NMR ($\mathrm{CDCl_3}$): δ 140.23, 125.53, 122.68, 120.36, 118.81, 108.51 (aryl), 44.94 ($\mathrm{SiC_2H_4}\mathit{C}\mathrm{H_2N}$), 22.18 ($\mathrm{SiCH_2}\mathit{C}\mathrm{H_2}$), 14.46 ($\mathrm{Si}\mathit{C}\mathrm{H_2C_2H_4N}$), −0.87 ($\mathrm{Si}\mathit{C}\mathrm{H_3}$). For $[\mathrm{Si(Me)(C_6H_{13})O}]_n$ 200 MHz ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.29 (m, 8H, $\mathrm{SiCH_2C_4}\mathit{H}_8\mathrm{CH_3}$), 0.88 (t, J = 6.4 Hz, 3H, $\mathrm{SiC_5H_{10}C}\mathit{H}_3$), 0.49 (t, J = 7.4 Hz, 2H, $\mathrm{SiC}\mathit{H}_2\mathrm{C_5H_{11}}$), −0.4 (s, 3H, $\mathrm{SiC}\mathit{H}_3$). 50 MHz ^{13}C NMR ($\mathrm{CDCl_3}$): δ 33.21, 31.75, 23.09, 22.71 ($\mathrm{SiCH_2}\mathit{C}_4\mathrm{H_8CH_3}$), 17.77 ($\mathrm{Si}\mathit{C}\mathrm{H_2C_5H_{13}}$), 14.13 ($\mathrm{SiC_5H_{10}}\mathit{C}\mathrm{H_3}$), −0.31 ($\mathrm{Si}\mathit{C}\mathrm{H_3}$). For $[\mathrm{Si(Me)(C_3H_6OC_2H_4OC_2H_4OCH_3)O}]_n$ 500 MHz ^{1}H ($\mathrm{CDCl_3}$): δ 3.58−3.46 (10 H, $\mathrm{OC}\mathit{H}_2$), 3.30 (3H, $\mathrm{OC}\mathit{H}_3$), 1.51 (br, 2H, $\mathrm{SiCH_2C}\mathit{H}_2\mathrm{CH_2O}$), 0.41 (br, 2H, $\mathrm{SiC}\mathit{H}_2$), −0.03 (s, 3H, $\mathrm{SiC}\mathit{H}_3$). 125 MHz ^{13}C NMR ($\mathrm{CDCl_3}$): δ 73.81, 71.76, 70.42, 70.35, 69.83 ($\mathrm{O}\mathit{C}\mathrm{H_2}$), 58.83 ($\mathrm{O}\mathit{C}\mathrm{H_3}$), 22.93 ($\mathrm{SiCH_2}\mathit{C}\mathrm{H_2CH_2O}$), 13.29 ($\mathrm{Si}\mathit{C}\mathrm{H_2}$), −0.58 ($\mathrm{Si}\mathit{C}\mathrm{H_3}$).

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