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Dehydrogenative Coupling of Substituted Phenylsilanes: Synthesis of Poly[((trifluoromethyl)phenyl)silanes]

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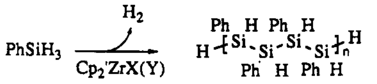
*Summary: The dehydrogenative coupling of substituted phenylsilanes $XC_6H_4SiH_3$ (X = p-CF_3 (**2a**), m-CF_3 (**2b**), o-CF_3 (**2c**), p-CH_3 (**3a**), m-CH_3 (**3b**), o-CH_3 (**3c**), H (**4**)) was carried out with $Cp_2Zr(Si(SiMe_3)_3)Me$ (**1b**). The molecular weight of the polymers produced ranged from 1000 to 3000 (vs polystyrene) with PDI = 1.5–2.4. Relative rates of polymerization for the substituted phenylsilanes were deduced by copolymerization reactions with phenylsilane.*

Introduction

Polysilanes are an intriguing class of radiation sensitive materials which absorb and fluoresce strongly in the ultraviolet.[1,2] This behavior has been attributed to low-lying σ–σ^* transitions from delocalized electronic states derived from σ-conjugated silicon atoms in the polymer backbone. The electronic properties of polysilanes are influenced by the molecular weight,[3–5] polymer conformation,[6] and substituents attached to the polymer backbone.[7,8]

The most common synthetic procedure for polysilanes is the condensation of chlorosilanes with alkali metals at elevated temperatures (Wurtz coupling).[9] Although this method affords high molecular weight materials, it is intolerant of many types of functional groups[7] and provides little control over the polymer stereochemistry.[10]

The strong influence of structure and functionality on the properties of these materials has stimulated a search for more selective synthetic strategies to these polymers. Significant developments include (1) Wurtz coupling in the presence of ultrasound at low temperature,[11] (2) the anionic polymerization of masked disilenes,[12,13] (3) the ring-opening polymerization of strained cyclic oligosilanes,[14,15] and (4) transition-metal mediated dehydrogenative coupling of hydrosilanes.[16–44] One of the more successful transition-metal routes involves the dehydrogenative coupling of phenylsilane in the presence of group 4 metallocene derivatives (eq 1).[18–43]



$$PhSiH_3 \xrightarrow[Cp_2'ZrX(Y)]{-H_2} H\!-\!\!\left[\overset{Ph}{\underset{H}{Si}}-\overset{H}{\underset{Ph}{Si}}-\overset{Ph}{\underset{H}{Si}}-\overset{H}{\underset{Ph}{Si}}\right]_n\!\!-\!H \qquad (1)$$

Cp' = cyclopentadienyl; ethylenebis(indenyl)
X = H, Cl, Alkyl
Y = Alkyl, H

A major drawback of the metallocene-catalyzed dehydrogenative coupling method is that the molecular weights of the resulting poly(phenylsilanes) are low.[33] Nevertheless, catalytic transition-metal mediated routes to silicon polymers provide the possibility of controlling the polymer

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Table I. Physical Characteristics of Monomers

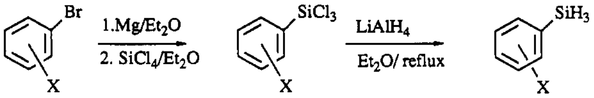
monomer	yield (%)	^{1}H NMR^a (ppm)	IR$_{Si-H}$ (cm^{-1})
p-$CF_3C_6H_4SiH_3$ (**2a**)	21	4.23	2166
m-$CF_3C_6H_4SiH_3$ (**2b**)	33	4.24	2167
o-$CF_3C_6H_4SiH_3$ (**2c**)	6	4.28^b	2176
p-$CH_3C_6H_4SiH_3$ (**3a**)	26	4.27, 2.05	2144
m-$CH_3C_6H_4SiH_3$ (**3b**)	32	4.32, 2.45	2155
o-$CH_3C_6H_4SiH_3$ (**3c**)	44	4.36, 2.59	2166
$C_6H_5SiH_3$ (**4**)	60	4.35	2166

^{a} All measurements were carried out with $CDCl_3$ as solvent. ^{b} Quartet; J = 5 Hz.

stereochemistry[24,45] as well as introducing functionality into the polymer.[46-48] In this contribution, we report that zirconocene derivatives are active catalysts for dehydrogenative coupling of ((trifluoromethyl)phenyl)silanes to poly[((trifluoromethyl)phenyl)silane].

Results

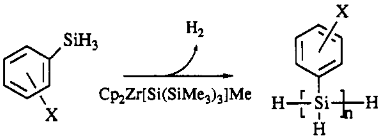
Monomer Synthesis. The phenylsilanes, **2a–c**, **3a–c**, **4**, were prepared in 6–60% overall yield by reduction of the corresponding phenyltrichlorosilane derivatives with $LiAlH_4$. (CAUTION: care should be exercised in the handling of phenylsilanes in the presence of $AlCl_3$; see Experimental Section).[49] The monomers, **2a–c**, **3a–c**, **4**, were purified by fractional distillation, degassed, and shown to be >95% pure by GC analysis (Table I). The phenyltrichlorosilanes were prepared via reaction of the appropriate phenyl Grignard reagents and $SiCl_4$ (eq 2).



(2)

X = CF_3, CH_3

Homopolymerization. The silylzirconocene complex $Cp_2Zr(Si(SiMe_3)_3)Me$[50] (**1b**) was investigated for the polymerization of the phenylsilane derivatives (eq 3). The Cp_2ZrCl_2/n-BuLi catalyst system[34,37,45,51-53] is also active for the polymerization of the substituted phenylsilanes but was less reproducible in kinetic experiments when compared to the Tilley initiator. Polymerization of the para- and meta-substituted phenylsilanes commenced immediately upon addition of the monomer to a catalyst solution of **1b**, as evidenced by the immediate release of hydrogen. The polymers were isolated as off-white or clear tacky materials which are soluble in most organic solvents. Table II summarizes the polymerization results. The ortho-substituted phenylsilane derivatives failed to yield any homopolymer under similar conditions.



(3)

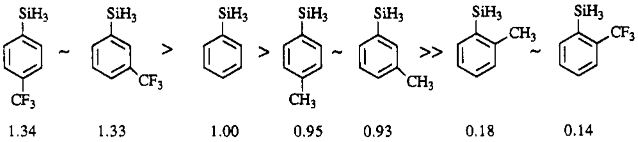
X = CF_3, CH_3, H

Table II. Polymerization of Substituted Phenylsilanes with $Cp_2Zr(Si(SiMe_3)_3Me^a$

monomer	yield (%)	[Si]$_0$	time (h)	mol wt^b M_w	M_n	PDI	% cyclics^c
p-$CF_3C_6H_4SiH_3$ (**2a**)	35	5.7	20	1540	630	2.42	0
m-$CF_3C_6H_4SiH_3$ (**2b**)	45	5.7	19	2600	1680	1.54	2.0
p-$CH_3C_6H_4SiH_3$ (**3a**)	60	5.7	22	1020	530	1.91	4.7
m-$CH_3C_6H_4SiH_3$ (**3b**)	99	5.7	19	1860	900	2.06	27.0
$C_6H_5SiH_3$ (**4**)	74	5.7	21	1860	800	2.34	18.0
m-$CF_3C_6H_4SiH_3$ (**2b**)	40	neat	41	2870	1720	1.66	2.4
m-$CH_3C_6H_4SiH_3$ (**3b**)	88	neat	41	1610	810	2.00	21.7
$C_6H_5SiH_3$ (**4**)	99	neat	14	2420	1000	2.42	7.0

^{a} [Zr] = 0.04 M; room temperature. ^{b} GPC vs polystyrene. ^{c} Determined by ^{1}H NMR by comparing the ratio of resonances above 5 ppm to those below 4.8 ppm.

Scheme I. Relative Rates of Polymerization



Secondary silane derivatives were very slow to polymerize under these conditions: only a trace amount of coupling products could be observed in the presence of 1 at room temperature.

The polymers reported here show no sign of cross-linking due to coupling of the $-CF_3$ group. A single resonance is observed in the ^{19}F NMR spectra of these materials at 109 ppm (external reference $CFCl_3$), consistent with the presence of a trifluoromethyl substituent. The molecular weight of the trifluoromethyl-substituted phenylsilanes (as determined by GPC) is similar to those of oligo(phenylsilanes) prepared under similar conditions. Investigation of the electronic properties of these polymers is currently underway and will be the subject of a future paper.

Copolymerizations. Copolymerization reactions of **2a–c**, **3a–c**, and phenylsilane **4** were performed in an attempt to estimate the relative rates of polymerization. The relative rates were measured by adding a precooled monomer solution to a 0 °C thermostated solution of $Cp_2Zr(Si(SiMe_3)_3)Me$ and monitoring the monomer conversion by GC. The relative rates of polymerization are given in Scheme I.

Discussion

The dehydrogenative coupling of hydrosilanes by transition-metal catalysts is a mild, room-temperature method for forming silicon–silicon bonds.[16-44] While the molecular weights of polymers produced by this method are lower than those produced via Wurtz coupling of dichlorosilanes, transition-metal mediated strategies are more tolerant of functional groups.

Previous efforts to incorporate trifluoromethyl substituents into polysilanes via Wurtz coupling were unsuccessful due to cross-linking of the trifluoromethyl substituents under the reaction conditions.[54] In contrast,

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dehydrogenative coupling of trifluoromethyl-substituted phenylsilanes occurs readily in the presence of zirconocene derivatives to yield low molecular weight, soluble polysilanes. The ^{19}F NMR results indicate that the polymers are not cross-linked via the CF_3 group in the presence of transition-metal catalysts. Although the molecular weights determined by GPC are not directly comparable for various substituted polysilanes, it appears that the polymers obtained from the trifluoromethyl-substituted phenylsilanes are approximately of the same degree of polymerization as those obtained from phenylsilane or the tolylsilanes.

The copolymerizations of phenylsilane and substituted phenylsilanes were carried out to get an estimate of the relative reactivity of the various monomers. Relative to phenylsilane, the *p*- and *m*-trifluoromethyl-substituted silanes react faster, while the *p*- and *m*-tolylsilanes react slower than phenylsilane. Substitution in the ortho position, however, results in slower rates for both the methyl and trifluoromethyl substituents. These results suggest that both steric and electronic effects influence the rate of arylsilane dehydrogenative coupling. The activating effect of electron-withdrawing groups had not been previously observed but is consistent with Harrod's previous observation that tolylsilane is slower than phenylsilane for the cohydrogenation of cyclohexene.[19] The slower rates of reaction for the more sterically hindered ortho-substituted phenylsilanes are consonant with the large steric effects expected for the σ-bond metathesis step-growth polymerization mechanism proposed by Tilley.[29,31-33,46,55]

Experimental Section

All operations involving air-sensitive materials were carried out in an inert atmosphere either in a glovebox or by using standard Schlenk-line techniques. All solvents were distilled under nitrogen prior to use: aromatic solvents and diethyl ether from sodium/benzophenone, pentane from $LiAlH_4$. Cp_2ZrCl_2 was purchased from Boulder Scientific and used as received. $(THF)_3LiSi(SiMe_3)_3$[56] and $Cp_2ZrSi(SiMe_3)_3Me$[50] were prepared according by literature methods. GC analyses were obtained on a Hewlett Packard 5890 chromatograph equipped with an SE 54 column (5% phenylmethylsilicone, 95% methylsilicone, 0.33 u × 0.2 mm × 25 m) in conjuction with a flame ionization or thermocouple detector. GC/MS data were obtained on an identical HP 5890 chromatograph connected to a Hewlett Packard 5970 mass selective detector. Analytical GPC data were obtained versus polystyrene standards on Waters 10^3- and 500-Å and Linear Ultrastyragel columns employing a Waters 410 refractive index diffractometer with THF as a solvent. Multinuclear NMR spectra were recorded on a Varian XL-400-MHz or Gemini 200-MHz instrument in deuterated chloroform or deuterated benzene with hexamethyldisilane or TMS as an internal reference. $CFCl_3$ was used as an external standard with the ^{19}F NMR spectra and chemical shifts are reported with reference to $CFCl_3$ = 0.0 ppm. Density calculations were determined by gravimetric methods. IR spectra were recorded on a Perkin-Elmer 1600 Series FT-IR. Elemental analyses were performed by E&R Microanalytical.

Monomer Synthesis. $p\text{-}CH_3C_6H_4SiH_3$ and $C_6H_5SiH_3$ were obtained directly from reduction of purchased phenylsilyl chlorides (Hüls America). The following procedure is representative of the other monomers. The monomer synthesis was completed in three steps: (1) formation of the Grignard reagent, (2) reaction of the Grignard reagent with $SiCl_4$, and (3) reduction with $LiAlH_4$. There are several **precautions** that must be taken during the synthesis. (1) The formation of the Grignard is slow, and care must be taken to ensure that the exothermic reaction does not run out of control. (2) In the absence of ether, *$AlCl_3$ catalyzed silane redistribution reactions occur which can result in formation of SiH_4,*[49] *an explosive gas when in contact with air. Therefore, the $LiAlH_4$ reduction of the silicon chlorides must be completed in ether and quenched properly with water prior to distillation.*

Synthesis of $m\text{-}CF_3C_6H_4SiH_3$ (2b). Grignard Formation. A 250-mL round bottom flask equipped with a reflux condenser and pressure equalizing addition funnel was charged with 5.8331 g (0.240 mol) of Mg and 100 mL of Et_2O. 3-(Trifluoromethyl)-bromobenzene (31 mL, 0.222 mol) was added to the addition funnel and diluted with 45 mL of Et_2O. Grignard formation was initiated by dropwise addition of the bromide to the suspended Mg solution. Upon formation of the Grignard reagent, the bromide was slowly added to maintain a gentle reflux. The color of the solution gradually darkens during the course of the reaction, resulting in a brown/black solution upon completion. After addition of the bromide, the solution was stirred at room temperature for 2 h.

Reaction of Grignard with $SiCl_4$. A 1000-mL round bottom flask was outfitted with a reflux condenser and pressure equalizing addition funnel. Then 175 mL of Et_2O and 105 mL of $SiCl_4$ (0.916 mol) were added to this flask. The Grignard reagent is then added to the addition funnel and slowly added to the $Et_2O/SiCl_4$ solution over the course of 30 min. After addition of the Grignard reagent, the solution is refluxed for 72 h. The reaction is cooled and filtered to remove the salts.

Reduction with $LiAlH_4$. A 30.173-g (0.795-mol) sample of $LiAlH_4$ was dissolved in 250 mL of Et_2O in a 1000-mL round bottom flask equipped with a reflux condenser and pressure equalizing addition funnel. The yellow $m\text{-}CF_3C_6H_4SiCl_3$ solution was added to the addition funnel. The addition of the chloride solution was completed dropwise over the course of 3 h. Gentle reflux was maintained during the addition. Upon completion of the addition, the solution was refluxed for 46 h. The solution was cooled and slowly quenched by addition of an acid/water solution (20 mL of concentrated HCl/150 mL of H_2O). (***Caution***: The formation of SiH_4 is possible under the reaction conditions.[49] Removal of ether in the presence of $AlCl_xH_{3-x}$ will catalyze the redistribution of phenylsilanes to SiH_4. The reaction must be quenched to remove any excess $AlCl_xH_{x-3}$ reagents prior to product isolation.) The Et_2O layer is extracted and concentrated. The solution is fractionally distilled at 30 mmHg/50 °C to yield 12.952 g (33% overall yield) of $m\text{-}CF_3C_6H_4SiH_3$. *d* (g/mL) = 1.192. ^1H NMR ($CDCl_3$): 7.84 (s, 1H, ArH), 7.76 (d, *J* = 7 Hz, 1H, ArH), 7.65 (d, *J* = 7 Hz, 1H, ArH), 7.47 (t, *J* = 7 Hz, 1H, ArH), 4.24 ppm (s, 3H, SiH). ^{13}C NMR ($CDCl_3$): 139.08, 132.24, 129.80, 128.37, 126.59, 125.46, 122.75 ppm. IR (neat): 3070, 2167, 1603, 1413, 1326, 1265, 1124, 1075, 917, 803, 704 cm^{-1}. Partial GC/MS data, *m/e* (relative intensity): M^+ = 176 (0.10), 175 (0.14), 128 (0.09), 127 (1.0), 108 (0.07), 107 (0.08), 77 (0.10). Anal. Calc: C, 47.7; H, 3.98. Found: C, 47.63; H, 4.00.

The secondary silane, $(m\text{-}CF_3C_6H_4)_2SiH_2$, can also be isolated from the crude reaction mixture. *d* (g/mL) = 0.7105. ^1H NMR ($CDCl_3$): 7.87–7.59 (m, 8H, ArH), 5.01 ppm (s, 2H, SiH). ^{13}C NMR ($CDCl_3$): 138.90, 132.04, 131.91, 128.65, 127.06 ppm. IR (near): 3059, 2155, 1412, 1336, 1129, 1075, 928, 846, 797, 699 cm^{-1}. Partial GC/MS data, *m/e* (relative intensity): M^+ = 320 (0.01), 319 ().06), 193 (0.15), 127 (1.0), 108 (0.70), 107 (0.12), 77 (0.09). Anal. Calc: C, 52.5; H, 3.13. Found: C, 52.78; H, 3.14.

$p\text{-}CF_3C_6H_4SiH_3$ (2a): 21% overall yield. *d* (g/mL) = 1.196. ^1H NMR ($CDCl_3$): 7.71 (d, *J* = 7 Hz, 2H, ArH), 7.60 (d, *J* = 7 Hz, 2H, ArH), 4.24 ppm (s, 3H, SiH). ^{13}C NMR ($CDCl_3$): 136.12, 133.41, 132.06, 125.40, 124.57, 122.69 ppm. IR (neat): 3081, 3037, 2166, 1396, 1320, 1156, 1124, 1058, 928, 830 cm^{-1}. Partial GC/MS data, *m/e* (relative intensity): M^+ = 176 (0.08), 175 (0.10), 128 (0.08), 127 (1.0), 107 (0.09), 77 (0.14). Anal. Calc: C, 47.7; H, 3.98. Found: C, 47.46; H, 3.97.

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(p-$CF_3C_6H_4)_2SiH_2$ can also be isolated from the crude reaction mixture. d (g/mL) = 0.8775. ^{1}H NMR ($CDCl_3$): 7.71 (d, J = 7 Hz, 4H), 7.63 (d, J = 7 Hz, 4H) 4.99 ppm (s, 2H, SiH). ^{13}C NMR ($CDCl_3$): 135.97, 135.41. 124.81, 122.61 ppm. IR (neat): 3256, 3037, 2155, 1608, 1391, 1167, 1129, 1058, 933, 851, 823, 701 cm^{-1}. Partial GC/MS data, m/e (relative intensity): M^+ = 319 (0.05), 193 (0.11), 127 (1.0), 108 (0.73), 107 (0.19), 77 (0.19), 75 (0.10), 57 (0.09), 51 (0.09). Anal. Calc: C, 52.5; H, 3.13. Found: C, 52.76; H, 3.01.

o-$CF_3C_6H_4SiH_3$ (2c): 6% overall yield. ^{1}H NMR ($CDCl_3$): 7.77–7.24 (m, 4H, ArH), 4.28 ppm (q, J = 5 Hz, 3H, SiH). ^{13}C NMR ($CDCl_3$): 138.67, 131.00, 130.24, 125.92 ppm. IR (neat): 3070, 2176, 1440, 1320, 1173, 1118, 1047, 922, 770 cm^{-1}. Partial GC/MS data, m/e (relative intensity): M^+ = 176 (0.06), $M^+ - SiH_3$ = 147 (0.02), 128 (0.08), 127 (1.0), $M^+ - CF_3$ = 107 (0.09), 89 (0.10), 77 (0.10) 65 (0.11), 63 (0.016).

p-$CH_3C_6H_4SiH_3$ (3a): 26% overall yield. d (g/mL) = 0.906. ^{1}H NMR ($CDCl_3$): 7.56 (d, J = 7 Hz, 2H, ArH), 7.25 (d, J = 7 Hz, 2H, ArH), 4.27 (s, 3H, SiH), 2.43 ppm (s, 3H, $ArCH_3$). ^{13}C NMR ($CDCl_3$): 139.79, 135.85, 128.96, 124.35, 21.48 ppm. IR (neat): 3037, 3016, 2155, 1113, 928, 802, 726 cm^{-1}. Partial GC/MS data, m/e (relative intensity): M^+ = 122 (0.40), 121 (0.28), 120 (0.13), 119 (0.14), $M^+ - CH_3$ = 107 (0.10), 105 (0.17), $M^+ - SiH_3$ = 91 (1.0), 65 (0.17). Anal. Calc: C, 68.8; H, 8.2. Found: C, 68.66; H, 8.26.

m-$CH_3C_6H_3SiH_3$ (3b): 32% overall yield. d (g/mL) = 0.906. ^{1}H NMR ($CDCl_3$): 7.44–7.24 (m, 4H ArH), 4.21 (s, 3H, SiH), 2.38 ppm (s, 3H, $ArCH_3$). ^{13}C NMR ($CDCl_3$): 137.52, 136.50, 132.83, 130.60, 128.05, 127.96, 21.33 ppm. IR (neat): 3016, 2918, 2166, 1478, 1402, 1222, 1118, 933, 781 cm^{-1}. Partial GC/MS data, m/e (relative intensity): M^+ = 122 (0.50), 121 (0.30), 120 (0.16), 119 (0.17), $M^+ - CH_3$ = 107 (0.13), 105 (0.20), $M^+ - SiH_3$ = 93 (0.18), 92 (0.14), 91 (1.0), 67 (0.12), 65 (0.13). Anal. Calc: C, 68.8; H, 8.2. Found: C, 69.0; H, 8.12.

o-$CH_3C_6H_4SiH_3$ (3c): 44% overall yield. d (g/mL) = 0.853. ^{1}H NMR ($CDCl_3$): 144.43, 137.10, 130.53, 129.19, 128.21, 125.30, 22.56 ppm. IR (neat): 3059, 3005, 2166, 1445, 1129, 928, 753, 726 cm^{-1}. Partial GC/MS data, m/e (relative intensity): M^+ = 122 (0.47), 121 (0.29), 120 (0.15), 119 (0.17), $M^+ - CH_3$ = 107 (0.13), 105 (0.21), $M^+ - SiH_3$ = 93 (0.18), 92 (0.14), 91 (1.0), 67 (0.14), 65 (0.17), 53 (0.29). Anal. Calcd: C, 68.8; H, 8.20. Found: C, 69.1; H, 7.9.

$C_6H_5SiH_3$ (4): 60% overall yield. d (g/mL) = 0.868. ^{1}H NMR ($CDCl_3$): 7.74–7.47 (m, 5H ArH), 4.35 ppm (s, 3H, SiH). IR (neat): 3070, 3016, 2166, 1429, 1118, 928, 699 cm^{-1}. Partial GC/MS data, m/e (relative intensity): M^+ = 108 (0.84), 107 (1.0), 106 (0.91), 105 (0.71), 81 (0.15), $M^+ - SiH_3$ = 79 (0.23), 78 (0.24), 77 (0.35), 55 (0.21), 54 (0.18), 53 (0.81), 52 (0.13), 51 (0.35).

Homopolymerization: Polymerization of 2b. The following procedure is representative of the homopolymerization reactions. A solution of catalyst **1b** (18 mg, 0.037 mmol in 0.19 mL of ethylbenzene) was prepared and cooled to 0 °C. To this was added via cannula 1.05 mL (7.11 mmol) of silane. Following immediate release of hydrogen gas, the reaction was warmed to room temperature and stirred for 19 h. After dilution with toluene (15 mL), Florisil was added to the reaction mixture. The mixture was filtered over a Florisil column. The column was rinsed 3 × 25 mL of toluene, and the combined toluene extracts were collected. Evaporation of solvent yielded 0.564 g (45% yield based on monomer) of tacky product. ^{1}H NMR (C_6D_6): 7.8–6.6 (m, ArH), 4.5–3.8 ppm (m, SiH). GPC: M_w = 2600; M_n = 1680; M_w/N_n = 1.54. Anal. Calcd: C, 48.3; H, 2.9. Found: C, 48.3; H, 2.9.

Poly(p-$CF_3C_6H_4SiH$): 35% yield. ^{1}H NMR (C_6D_6): 7.7–6.7 (m, ArH), 4.5–4.0 ppm (m, SiH). ^{19}F NMR (C_6D_6): 109 ppm. GPC: M_w = 1540; M_n = 630; M_w/M_n = 2.42.

Poly(m-$CH_3C_6H_4SiH$): 99% yield. ^{1}H NMR (C_6D_6): 7.8–6.7 (m, ArH), 5.5–4.0 (m, SiH), 2.3–1.7 ppm (m, $ArCH_3$). GPC: M_w = 1860; M_n = 900; M_w/M_n = 2.06. Anal. Calcd: C, 70.0; H, 6.7. Found: C, 70.2; H, 6.8.

Poly(p-$CH_3C_6H_4SiH$): 60% yield. ^{1}H NMR (C_6D_6): 7.7–6.7 (m, ArH), 5.0–4.5 (m, SiH), 2.2–1.9 ppm (m, $ArCH_3$). GPC: M_w = 1020; M_n = 530; M_w/M_n = 1.91.

Poly(C_6H_5SiH): 74% yield. ^{1}H NMR (C_6D_6): 7.8–6.6 (m, ArH), 5.2–4.0 ppm (m, SiH). GPC: M_w = 1860; M_n = 800; M_w/M_n = 2.34.

Copolymerizations. The following procedure is representative of the copolymerization reactions.

Copolymerization of $PhSiH_3$ (4) and m-$CF_3C_6H_4SiH_3$ (2b). A Schlenk tube was charged with 2 mL of 70 mM catalyst solution and 4 mL of toluene. A monomer solution was prepared consisting of 0.68 g of $PhSiH_3$ (4) (6.3 mmol), 1.11 g of m-$CF_3C_6H_4SiH_3$ **(2b)** (6.3 mmol), and 0.50 g of ethylbenzene (4.72 mmol). Toluene was added to bring the total volume to 5 mL. The catalyst solution and the monomer solution were cooled to 0 °C. At 0 °C, 4 mL of the monomer solution was added to the catalyst solution. GC aliquots were removed at timed intervals, eluted through a short Florisil column to remove catalyst residue, and injected into the GC. Samples were analyzed using ethylbenzene as an internal standard.

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