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Polycondensation of Diarylsilanes with Aromatic Dithiols and the Model Reaction Involving $RhCl(PPh_3)_3$-Catalyzed Si−S Bond Formation

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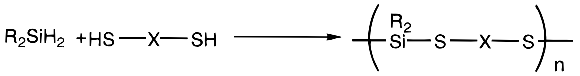
Summary: Polymerization of Ar_2SiH_2 (Ar = Ph, p-MeC_6H_4, and m-MeC_6H_4) with 1,3- and with 1,4-benzenedithiol proceeds at 90−110 °C to give the polymers $-[(SiAr_2)-S-C_6H_4-S-]_n-$ with M_w values in the range $(1.5-7.0) \times 10^3$, based on a polystyrene standard.

Introduction

Transition metal complex catalyzed formation of silicon−heteroatom bonds has been developed to synthesize polymers or oligomers containing these bonds in the main chain. Transition metal complex catalyzed dehydrocoupling of hydrosilanes with amines or ring opening reactions of cyclic oligosilazanes gives linear or cross-linked poly(silazane) compounds that are regarded as precursors for silicon nitride.[2−6] The Pd complex catalyzed reaction of cyclic oligosilanes and benzoquinone gives novel polymers containing Si−O bonds in the main chain.[7] On the other hand, organic polymers containing Si−S bonds have attracted much less attention than those having Si−O and Si−N bonds.[8] This is partly due to the tendency of the Si−S bond to undergo hydrolysis by atmospheric moisture and to the scarcity of Si−S bond-forming reactions suited for the synthesis of polymers. Dehydrocoupling of a diorganosilane with a dithiol would provide novel polymers having Si−S bonds in the main chain according to Scheme 1. Ojima et al. have previously reported $RhCl(PPh_3)_3$-catalyzed dehydrocoupling of hydrosilanes with equimolar amounts of thiols to give the corresponding (thiolato)hydrosilanes[9] (eq 1). This Si−S bond-forming reaction proceeds smoothly under mild conditions and does not require aqueous workup or addition of base.[10−12]

$$R_2SiH_2 + R'SH \xrightarrow[RhCl(PPh_3)_3\ \text{cat.}]{\text{neat, r. t.}} R_2SiH(SR') + H_2 \quad (R' = Et, Ph) \qquad (1)$$

Scheme 1



$$R_2SiH_2 + HS-X-SH \longrightarrow -\!\left(\overset{R_2}{Si}-S-X-S\right)_n\!-$$

Formation of polymers containing alternating diorganosilylene and organic dithiyl units in the main chain by the Rh-catalyzed dehydrocoupling requires that the diorganosilanes react readily with 2 equiv of SH groups to cause substitution of both SiH hydrogens by thiolato groups and that the Si−S bond-forming reaction proceeds much faster than the potentially competing dehydrocoupling to form Si−Si bonds.[13,14] We have examined utility of reaction 1 for the preparation of bis- or tris(thiolato)silanes and for the polymerization of diorganosilanes with dithiols. In this paper we report results of $RhCl(PPh_3)_3$-catalyzed reactions of diphenylsilane and phenylsilane with an excess of aromatic thiols as well as the polymerization of diarylsilanes with benzenedithiol to give the polymers containing Si−S bonds in the main chain.

Results and Discussion

Preparation and Structure of Bis- or Tris(thiolato)silanes. Reactions of Ph_2SiH_2 with 2 equiv of PhSH and *p*-MeC_6H_4SH at room temperature in the presence of $RhCl(PPh_3)_3$ catalyst give $Ph_2Si(SPh)_2$ (**1**) and $Ph_2Si(SC_6H_4$-*p*-$Me)_2$ (**2**), respectively, at room temperature (eq 2). Reaction of Ph_2SiH_2 with the sterically hindered *o*-MeC_6H_4SH also proceeds smoothly to give $Ph_2Si(SC_6H_4$-*o*-$Me)_2$, (**3**), in high yield (84%). The ^1H NMR and IR spectra of the products agree with the above formula.

$$Ph_2SiH_2 + 2\,ArSH \xrightarrow[RhCl(PPh_3)_3\ \text{cat.}]{} Ph_2Si(SAr)_2 + 2\,H_2 \qquad (2)$$

1 : Ar = C_6H_5,
2 : Ar = *p*-MeC_6H_4,
3 : Ar = *o*-MeC_6H_4.

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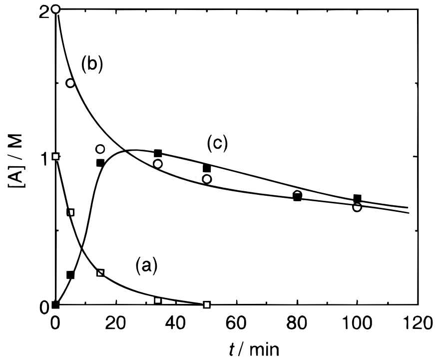


Figure 1. Change of concentration ([A]/M) of (a) Ph_2SiH_2, (b) PhSH, and (c) $Ph_2SiH(SPh)$ during the reaction of Ph_2SiH_2 with 2 equiv of HSPh at room temperature in toluene in the presence of $RhCl(PPh_3)_3$ (0.2 mol % of Ph_2SiH_2).

Scheme 2

$$Ph_2SiH_2 \xrightarrow{+\ ArSH} Ph_2SiH(SAr) \xrightarrow{+\ ArSH} Ph_2Si(SAr)_2$$

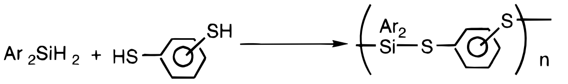
Gas chromatographic analysis of the reaction mixture of Ph_2SiH_2 and 2 equiv of PhSH in the presence of $RhCl(PPh_3)_3$ catalyst (1.2 mol % of Ph_2SiH_2) indicates immediate disappearance of Ph_2SiH_2 accompanied by formation of $Ph_2SiH(SPh)$, whose yield rises to 84% after a reaction time of 5 min. $Ph_2SiH(SPh)$ is completely consumed by further reaction within 2 h under the conditions. The main final product is $Ph_2Si(SPh)_2$ as isolated although it could not be analyzed by GC due to its low volatility. A small amount of PhSH (3 mol % of initial Ph_2SiH_2) remains unreacted even after consumption of $Ph_2SiH(SPh)$ possibly due to minor side reaction such as dehydrocoupling of two Si−H groups. However, the products due to the side reactions are not well characterized. Figure 1 shows the results of the GC analysis of the reaction mixture containing $RhCl(PPh_3)_3$ catalyst in a smaller amount (0.2 mol %). The reaction causes initial formation of $Ph_2SiH(SPh)$ which undergoes slow reaction with PhSH to give $Ph_2Si(SPh)_2$. These results indicate that reaction (2) proceeds via a stepwise pathway, as shown in Scheme 2. The former reaction is much faster than the latter although the whole reaction is completed in 2 h at room temperature when 1.2 mol % of $RhCl(PPh_3)_3$ catalyst is used. This observation led to development of the following synthesis of mixed (thiolato)diphenylsilanes. Reaction of Ph_2SiH_2 with equimolar amounts of PhSH in the presence of $RhCl(PPh_3)_3$ catalyst, followed by addition of equimolar $p\text{-}MeC_6H_4SH$, proceeds smoothly to give $Ph_2Si(SPh)(SC_6H_4\text{-}p\text{-}Me)$ (**4**) as a light yellow oil in 63% yield. The ^1H NMR spectrum and analytical data for **4** agree with the above formula.

Reactions of $PhSiH_3$ with 3 equiv of arenethiols catalyzed by $RhCl(PPh_3)_3$ give the corresponding tris(thiolato)phenylsilanes, $PhSi(SPh)_3$ (**5**), $PhSi(SC_6H_4\text{-}p\text{-}Me)_3$ (**6**), and $PhSi(SC_6H_4\text{-}o\text{-}Me)_3$ (**7**), at room temperature (eq 3). The lower yield of **7** (36%) compared to those of **5** (74%) and **6** (88%) can be attributed to steric hindrance of the methyl groups on the phenyl ring. Figure 2 shows molecular structures of **6** determined by X-ray crystallography.[15] Si−S bond lengths of the compounds are in the range 2.126−2.133 Å, which are similar to or somewhat shorter than those of already reported Si−S bond-containing compounds.[16−20]

$$PhSiH_3 + 3\ ArSH \xrightarrow[RhCl(PPh_3)_3\ \text{cat.}]{} PhSi(SAr)_3 + 3\ H_2 \qquad (3)$$

5 : Ar = C_6H_5,
6 : Ar = $p\text{-}MeC_6H_4$,
7 : Ar = $o\text{-}MeC_6H_4$.

Rh Complex Catalyzed Polycondensation of Diarylsilanes with 1,3- and 1,4-Benzenedithiol. Polycondensation of diarylsilanes with 1,3- and 1,4-benzenedithiol is carried out by heating the equimolar mixtures at 90−110 °C in the presence of $RhCl(PPh_3)_3$ catalyst (eq 4). Table 1 summarizes results of polycondensation of Ph_2SiH_2, $(p\text{-}MeC_6H_4)_2SiH_2$, and $(m\text{-}MeC_6H_4)_2SiH_2$ with 1,3- and 1,4-benzenedithiols. The products are obtained as yellow to brown solids which are soluble in toluene and $CHCl_3$ and insoluble in hexane and acetone. Polymer yields are not high partly because the reaction mixture contains considerable amounts of low molecular weight oligomers, which are removed from the product by washing with hexane or acetone. Polymer **8** is stable enough to keep the analytical value unchanged for 2 months in the solid state but undergoes degradation in toluene solution to give trisiloxane, $(Ph_2SiO)_3$, probably due to hydrolysis by aerial moisture. Figure 3 shows GPC traces of **9** obtained from the reaction of Ph_2SiH_2 and 1,4-benzenedithiol. The reaction mixture after stirring for 24 h at room temperature shows the GPC trace that agrees with two components having low molecular weights. The reactions for 4 h and for 18 h at 100 °C give the polymer products which are isolated in similar yields and show GPC traces similar to each other with M_w value of 2.3×10^3. The results indicate that the polycondensation proceeds smoothly at 100 °C but ceases after 4 h. Polycondensation of other substrates (entries 1, 4−6) is also completed in 4 h, while further heating the reaction mixture of $(p\text{-}MeC_6H_4)_2SiH_2$ with 1,3-benzenedithiol for 14 h causes increases in the molecular weight of the product from 0.8×10^3 to 3.0×10^3.



(4)

8 : Ar = Ph, 1,3-benzenedithiol;
9 : Ar = Ph, 1,4-benzenedithiol;
10 : Ar = $p\text{-}MeC_6H_4$, 1,3-benzenedithiol;
11 : Ar = $p\text{-}MeC_6H_4$, 1,4-benzenedithiol;
12 : Ar = $m\text{-}MeC_6H_4$, 1,3-benzenedithiol;
13 : Ar = $m\text{-}MeC_6H_4$, 1,4-benzenedithiol

In summary we have shown that $RhCl(PPh_3)_3$-catalyzed dehydrocoupling of SiH and SH groups introduces of two or three thiolato groups on the silicon atom by dehydrocoupling of hydrosilanes with thiols. Al-

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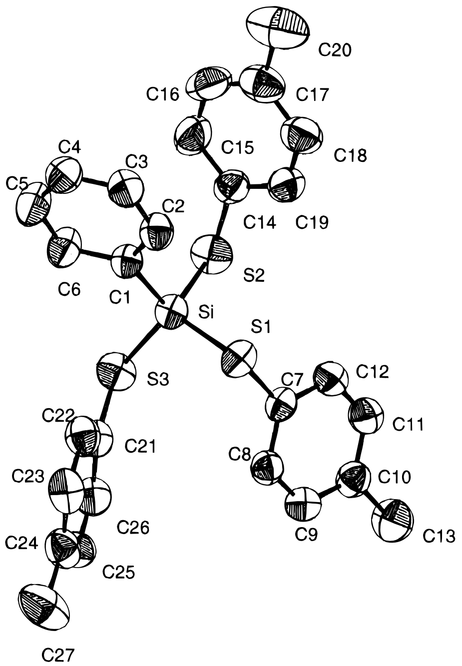

Figure 2. ORTEP drawing of PhSi(SC$_6$H$_4$-p-Me)$_3$ (**6**) at the 50% ellipsoidal level. Selected bond distances (Å) and angles (deg): Si1−C1, 1.863(1); Si1−S1, 2.130(1); Si1−S2, 2.132(1); Si1−S3, 2.126(1); S1−C7, 1.780(2); S2−C14, 1.786(2); S3−C21, 1.785(2); C1−Si1−S1, 104.57(5); C1−Si1−S2, 110.23(5); C1−Si1−S3, 115.78(4); S1−Si1−S2, 113.98(2); S2−Si1−S3, 97.90(3); S1−Si1−S3, 114.66(2); Si1−S1−C7, 102.63(5); Si1−S2−C14, 98.54(6); Si1−S3−C21, 106.37(5).

though the reaction proceeds through stepwise displacement of the hydrogens on the Si atom by the thiolato groups, it is completed in a short period under mild conditions. The Rh complex catalyzed dehydrocoupling has enabled synthesis of novel polymers containing Si−S bonds in the main chain.

Experimental Section

General Procedure, Materials, and Measurements. All the manipulations of the complexes were carried out under nitrogen or argon atmosphere using standard Schlenk flasks. The solvents were dried in a usual manner, distilled, and stored under argon. Ph$_2$SiH$_2$, PhSiH$_3$, and 1,3- and 1,4-benzenedithiols were purchased from Tokyo Kasei Co. (*p*-MeC$_6$H$_4$)$_2$SiH$_2$ and (*m*−MeC$_6$H$_4$)$_2$SiH$_2$ were prepared by LiAlH$_4$ reduction of the corresponding dichlorodiarylsilane. RhCl(PPh$_3$)$_3$ was prepared according to the literature.[21] The monomers used for polymerization have been purified by distillation prior to use. IR spectra were obtained by a JASCO R810 spectrometer. NMR spectra (^{1}H and ^{13}C) were recorded on JEOL EX-90 and GX-500 spectrometers. GC and GC-MS measurements were carried out on Shimadzu 8A and Hitachi M-80 instruments, respectively, using a column packed with OV-1. GPC traces were obtained by a Shimadzu LC-9A HPLC equipped with an RI detector using CHCl$_3$ as eluent. The molecular weights were determined by using polystyrene as the standard. Elemental analyses were carried out by a Yanagimoto Type MT-2 CHN autocorder and a Yazawa halogen and sulfur analyzer.

Preparation of Ph$_2$Si(SPh)$_2$ (1), Ph$_2$Si(SC$_6$H$_4$-*p*-Me)$_2$ (2), and Ph$_2$Si(SC$_6$H$_4$-*o*-Me)$_2$ (3). A mixture of Ph$_2$SiH$_2$ (360 mg, 2.0 mmol), PhSH (470 mg, 4.3 mmol), and RhCl(PPh$_3$)$_3$ (40 mg, 0.043 mmol) in toluene (2 mL) was stirred at room temperature. GC analysis of the reaction mixture after 1 h of stirring showed consumption of Ph$_2$SiH$_2$. Further stirring overnight caused formation of a dark orange solution. Evaporation of the solvent under reduced pressure followed by addition of a mixture of toluene (0.5 mL) and hexane (ca. 50 mL) causes precipitation of a small amount of brown solid which was removed by filtration. Evaporation of the solvent from the filtrate gave **1** as a light yellow oil which crystallized on standing at −20 °C for 12 h (600 mg, 75%). ^{1}H NMR (CDCl$_3$, 90 MHz): δ = 7.8−6.8 (m). ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz): δ = 135.3, 135.1, 132.1, 130.7, 128.7, 127.9, 127.2, 125.4. Anal. Calcd for C$_{24}$H$_{20}$S$_2$Si: C, 72.0; H, 5.0. Found: C, 72.4; H, 5.2.

Similar reaction of Ph$_2$SiH$_2$ with *p*-MeC$_6$H$_4$SH gave **2** (73%). ^{1}H NMR (CDCl$_3$, 90 MHz): δ = 7.8−6.6 (m, 18H), 2.00 (s, 6H). ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz): δ = 137.0, 135.0, 134.8, 132.3, 130.2, 129.2, 127.7, 125.2, 20.8. Anal. Calcd for C$_{26}$H$_{24}$S$_2$Si: C, 72.9; H, 5.6; S, 15.0. Found: C, 73.4; H, 5.7; S, 14.1. Compound **3** was obtained analogously and purified by a short Florisil column (84%). ^{1}H NMR (CDCl$_3$, 90 MHz): δ = 7.8−6.6 (m, 18H), 2.00 (s, 6H). ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz): δ = 141.8, 135.8, 135.0, 134.2, 132.0, 130.4, 130.2, 128.9, 127.2, 125.8, 20.8. Anal. Calcd for C$_{26}$H$_{24}$S$_2$Si: C, 72.9; H, 5.6; S, 15.0. Found: C, 72.9; H, 5.7; S, 15.0.

Preparation of Ph$_2$Si(SPh)(SC$_6$H$_4$-*p*-Me) (4). A mixture of Ph$_2$SiH$_2$ (360 mg, 2.0 mmol), PhSH (220 mg, 2.0 mmol), and RhCl(PPh$_3$)$_3$ (20 mg, 0.022 mmol) in toluene (1 mL) was stirred at room temperature. Initial vigorous hydrogen evolution ceased after 10 min of stirring. HSC$_6$H$_4$-*p*-Me (250 mg, 2.0 mmol) was added to the reaction mixture to cause hydrogen evolution. After further stirring for 12 h, the mixture was passed through a short Florisil column using hexane (25 mL) as eluent to remove catalyst. Concentration of the eluent under reduced pressure gave **4** as a light yellow oil (520 mg, 63%). ^{1}H NMR (CDCl$_3$, 90 MHz): δ = 7.8−6.8 (m, 19H), 2.00 (s, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz): δ = 137.0, 135.3, 135.0, 134.9, 132.4, 130.6, 129.5, 128.5, 127.9, 127.2, 125.5, 125.4, 21.0. Anal. Calcd for C$_{25}$H$_{22}$S$_2$Si: C, 72.4; H, 5.3; S, 15.5. Found: C, 72.5; H, 5.3; S, 14.5.

Preparation of PhSi(SPh)$_3$ (5), PhSi(SC$_6$H$_4$-p-Me)$_3$ (6), and PhSi(SC$_6$H$_4$-*o*-Me)$_3$ (7). A mixture of PhSiH$_3$ (220 mg, 2.0 mmol), PhSH (660 mg, 6.0 mmol), and RhCl(PPh$_3$)$_3$ (30 mg, 0.032 mmol) in hexane (5 mL) was stirred for 12 h at room temperature. The reaction mixture was diluted with hexane (30 mL), and the resulting solution was filtered to remove the catalyst. Evaporation of the solvent under reduced pressure followed by recrystallization of the resulting semisolid from a minimum amount of hexane gave **5** as colorless crystals (640 mg, 74%). ^{1}H NMR (CDCl$_3$, 90 MHz): δ = 7.8−7.1 (m). ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz): δ = 135.0, 134.7, 131.9, 131.0, 128.8, 128.5, 127.8, 127.5. Anal. Calcd for C$_{24}$H$_{20}$S$_3$Si: C, 66.6; H, 4.7. Found: C, 66.4; H, 4.7.

Similar reactions of PhSiH$_3$ with HSC$_6$H$_4$-*p*-Me and with HSC$_6$H$_4$-*o*-Me gave PhSi(SC$_6$H$_4$-*p*-Me)$_3$ (**6**) (88%) and PhSi(SC$_6$H$_4$-*o*-Me)$_3$ (36%), respectively. ^{1}H NMR (**6**, CDCl$_3$, 90 MHz): δ = 8.0−6.7 (m, 17H), 1.90 (s, 9H). ^{13}C{^{1}H} NMR (**6**, CDCl$_3$, 125 MHz): δ = 137.4, 134.9, 134.8, 132.3, 130.8, 129.6, 127.8, 125.0, 30.9. Anal. Calcd for C$_{27}$H$_{26}$S$_3$Si: C, 68.3; H, 5.5; S, 20.3. Found for **6**: C, 68.7; H, 5.2; S, 19.8. ^{1}H NMR (**7**, CDCl$_3$, 90 MHz): δ = 7.8−6.9 (m, 17H), 2.00 (s, 9H). ^{13}C{^{1}H} NMR (**7**, CDCl$_3$, 125 MHz): δ = 136.0, 134.6, 134.2, 131.6, 129.4, 129.1, 128.2, 126.8, 30.9. Anal. Calcd for C$_{27}$H$_{26}$S$_3$Si: C, 68.3; H, 5.5; S, 20.3. Found for **7**: C, 67.7 ; H, 5.5; S, 20.2.

Polymerization of Ph$_2$SiH$_2$ with 1,3- and with 1,4-Benzenedithiol. To a mixture of Ph$_2$SiH$_2$ (180 mg, 0.98 mmol) and 1,3-benzenedithiol (140 mg, 0.98 mmol) was added RhCl(PPh$_3$)$_3$ (10 mg, 0.010 mmol) at room temperature. The reaction mixture was stirred in an oil bath at 90 °C for 6 h. An orange paste product was washed with Et$_2$O (10 mL × 2) to remove the remaining monomer and low molecular weight oligomer. The residual product was dried under high vacuum

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Table 1. Polymerization of Diarylsilane with Benzenedithiol

			conditions[a]			molecular weight[b]		anal. (%)[c]		
entry	diarylsilane	dithiol	temp (°C)	time (h)	yield (%)	M_w	M_n	C	H	S
1	Ph_2SiH_2	1,3-HSC_6H_4SH	110	3	67	3.0	2.7 (1.1)	66.1	4.1	19.7
								(67.0	4.3	19.9)
2	Ph_2SiH_2	1,4-HSC_6H_4SH	100	4	56	2.3	1.3 (1.8)	66.5	4.0	20.6
								(67.0	4.3	19.9)
3	(p-$MeC_6H_4)_2SiH_2$	1,3-HSC_6H_4SH	100	18	29	7.0	5.4 (1.3)	68.2	5.1	18.3
								(68.5	5.1	18.3)
4[d]	(p-$MeC_6H_4)_2SiH_2$	1,4-HSC_6H_4SH	90	4	37	1.5	1.4 (1.1)	68.6	5.2	18.6
								(68.5	5.1	18.3
5	(m-$MeC_6H_4)_2SiH_2$	1,3-HSC_6H_4SH	90	4	46		e	67.8	5.3	18.9
								(68.5	5.1	18.3)
6	(m-$MeC_6H_4)_2SiH_2$	1,4-HSC_6H_4SH	90	4	46	2.9	2.3[f] (1.3)	66.5	4.8	18.6
								(68.5	5.1	18.3)

[a] Reactions were carried out without solvent in the presence of 1 mol % $RhCl(PPh_3)_3$ unless otherwise stated. [b] Obtained by GPC vs polystyrene standard. Polydispersity is shown in parentheses. [c] Calculated values are in parentheses. [d] Reactions were carried out in toluene. [e] GPC pattern is complicated, and tops of the peaks are in the range $(0.7-0.3) \times 10^3$ (M_w value). [f] The product contains a small amount of the component with the lower molecular weight of M_w = ca. 700.

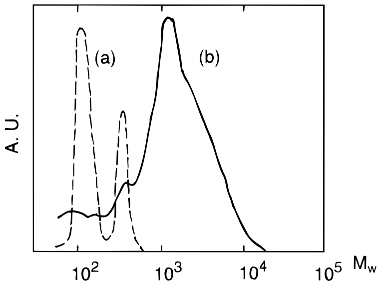

Figure 3. GPC traces of (a) the reaction mixture of Ph_2SiH_2 with 1,4-benzenedithiol at room temperature for 24 h and (b) $-[SiPh_2-S-p-C_6H_4-S-]_n-$ (**9**) isolated from the product of the reaction at 100 °C for 18 h.

to give $-[(SiPh_2)-S-m-C_6H_4-S-]_n-$ (**8**) as a yellowish brown solid (210 mg, 67%). ^1H NMR ($CDCl_3$, 90 MHz): $\delta = 7.9-6.5$. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 135.2, 134.5, 133.9, 131.5, 130.9, 129.9, 128.0, 127.9. The polymer product seems to contain a small amount of catalyst that is not removed during the above procedure. Although reprecipitaion of the polymer was attempted to obtain catalyst-free product, the ^{13}C NMR spectra revealed partial decomposition of the polymer during the reprecipitaion procedure.

Other polymers were prepared analogously. NMR data for **9** are as follows. ^1H NMR ($CDCl_3$, 90 MHz): $\delta = 7.8-7.0$. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 135.2, 134.6, 134.5, 132.2, 130.9, 129.5, 128.4, 128.0, 127.8. NMR data for **10** are as follows. ^1H NMR ($CDCl_3$, 90 MHz): $\delta = 7.9-6.8$ (m, 12H), 2.20 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz}: δ = 140.7, 138.9, 129.9, 128.7, 128.2, 21.5. NMR data for **11** are as follows. ^1H NMR ($CDCl_3$, 90 MHz} δ: $= 7.8-6.8$ (m, 12H), 2.20 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 140.9, 135.3, 135.1, 128.9, 128.6, 128.4, 21.6. NMR data for **12** are as follows. ^1H NMR ($CDCl_3$, 90 MHz): $\delta = 7.9-6.8$ (m, 12H), 2.20 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 137.4, 135.6, 135.0, 132.4, 131.6, 128.6, 127.8, 21.5. NMR data for **13** are as follows. ^1H NMR ($CDCl_3$, 90 MHz): $\delta = 8.0-6.8$ (m, 12H), 2.20 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 140.8, 137.3, 135.7, 133.7, 132.3, 131.5, 130.1, 129.3, 21.0.

X-ray Crystallography. Single crystals of **5** and **6** for X-ray crystallography were grown from hexane solutions by slow evaporation of the solvent. Crystal data and details of structure refinement are summarized in Table 2. Cell constants were refined by least-squares calculations of the setting angles of 25 reflections with 19° < 2θ < 22°. Intensities were collected on a Rigaku AFC-5 automated four-cycle diffractometer at 25 °C. Structure calculations were carried out by using the program system CRYSTAN on a FACOM A-70 computer. Atomic scattering factors were taken from the literature.

Table 2. Crystal Data and Details of Structure Refinement

	5	6
formula	$C_{24}H_{20}S_3Si$	$C_{27}H_{26}S_3Si$
M_r	432.66	474.77
cryst size (mm × mm × mm)	0.40 × 0.40 × 0.50	0.50 × 0.70 × 0.80
cryst system	monoclinic	monoclinic
space group	$P2_1$	$C2/c$
a (Å)	12.040(5)	16.639(4)
b (Å)	10.493(3)	12.880(4)
c (Å)	9.219(2)	23.906(10)
β (deg)	104.61(2)	90.53(3)
V (Å^3)	1117	5123
Z	2	8
T (°C)	25	25
λ (Å)	0.710 69	0.710 69
d_{calcd} (g cm^{-1})	1.291	1.232
μ (cm^{-1})	3.78	3.35
F(000)	452	2000
R	0.032	0.047
R_w[a]	0.032	0.046
no. of variables	312	358
no. of measd reflcns	2064	5070
no. of reflcns used ($I > 3\sigma(I)$)	1866	4075

[a] $w = [\sigma(F_o)]^{-2}$.

The structures were solved by a combination of direct methods and Fourier techniques. Full-matrix least-squares calculations were applied by using anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were located at idealized positions with isotropic temperature factors and included in least-squares calculation without refinement of the parameters.

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Supporting Information Available: Tables of atomic coordinates and B values, anisotropic thermal factors, and all the bond distances and angles of **5** and **6** and an ORTEP drawing of **5** (17 pages). Ordering information is given on any current masthead page.

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