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Borane-Catalyzed Si−H Activation Routes to Polysilanes Containing Thiolato Side Chains

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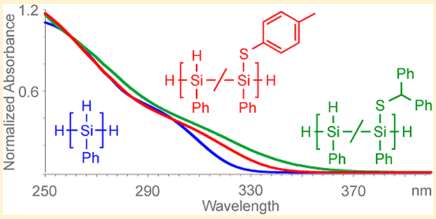
Ⓢ *Supporting Information*

ABSTRACT: Dehydrocoupling and hydrosilation reactions of the Si−H bonds in poly(phenylsilane) catalyzed by $B(C_6F_5)_3$ allow the preparation of new polymers containing both Si−H and Si−SR side chains. This postpolymerization modification takes place without any observable competing Si−Si bond cleavage, unlike other Lewis acid, transition-metal, or radical mediated routes. The −SR-functionalized polymers have been characterized by GPC, IR, UV−vis, elemental analysis, and ^{1}H, ^{13}C, and ^{29}Si NMR.



Polysilanes continue to be of interest for their intriguing electronic and optical properties,[1] which arise from σ conjugation along their all-Si backbones.[2] Practical application of these intriguing materials in device technologies remains undeveloped, however, because of the facile oxidative and photolytic degradation of the catenated silicon chains.[1g,2b,3] Our interest in designing more stable polysilane architectures has focused on catalytic dehydrocoupling routes to oligo- and polysilanes that contain Si−H bonds in the repeat units,[4] on the premise that the enormous, established arsenal of organic Si−H activation chemistry[5] could then be exploited in postpolymerization modification reactions. This would allow the introduction of considerably more structural variety than is possible via the standard reductive coupling routes to polysilanes.[6] We are not the first to exploit this Si−H activation route to modified polysilanes,[7] and Si−Ph cleavage strategies have also been reported.[8] However, the parent polysilanes are notoriously sensitive to Si−Si bond cleavage under most conditions of modification,[9] which can lead to reduced molecular weights (MWs).[10] For example, we found that previously reported radical,[7a−c] titanocene,[7g,h] and platinic acid mediated[9] Si−H activation methods gave moderate to significant Si−Si bond scission at poly(phenylsilane) (H−[Si(H)-Ph]$_n$−H) and even at more robust 1,2-dihydrodisilanes such as *sym*-tetraphenyldisilane.[11a,c] However, we have found that hydrosilation and heterodehydrocoupling reactions of disilanes mediated by $B(C_6F_5)_3$[12] proceed under mild conditions with absolute chemoselectivity for Si−H versus Si−Si activation to give new Si−O- and Si−S-containing substituents.[11a,b] In this communication we report the successful extension of this methodology to chemoselective postpolymerization modification of poly(phenylsilane) to introduce thiolato side chains.

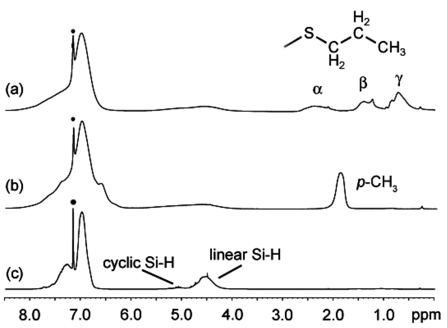


Figure 1. 500 MHz ^{1}H NMR spectra for (a) the −SPr^n modified polymer, (b) the −STol^p modified polymer, and (c) the parent poly(phenysilane), in d_6-benzene. The ● denotes residual C_6D_5H.

Addition of $B(C_6F_5)_3$ to a mixture of poly(phenylsilane)[13] and either HSPr^n or HSTol^p in toluene caused immediate bubbling, presumably due to evolution of hydrogen (Scheme 1, top). The resulting modified polymers were isolated as white or off-white solids, after trituration of the residues with either pentane or hexanes. The incorporation of new *n*-propyl- or *p*-tolylthiolato side chains in these polymers is evident from their ^{1}H NMR spectra (Figure 1), which show broad peaks ($\omega_{1/2}$ = 50−140 Hz) corresponding to the alkyl protons in these side chains, and broadening and increased complexity in the aromatic region, relative to the spectrum for the precursor poly(phenylsilane). Integration of the alkyl and Si−H regions of the ^{1}H NMR spectra allows a crude estimation of the degree of Si−H substitution: the modified polymers contain approximately 15−40% thiolato side chains.[14] IR spectroscopy provides qualitative confirmation of the partial replacement of Si−H bonds with Si−SR fragments in the modified polysilanes: the intensity of the $\nu_{\text{Si−H}}$ band at around 2100 cm^{-1} relative to the intensity of the $\nu_{\text{C−H}}$ band at around 3000 cm^{-1} is diminished, relative to the spectrum for the parent poly(phenylsilane). More critically, we observe weak absorptions at approximately 490−500 cm^{-1} in spectra for the SR-substituted polysilanes that are absent in spectra of the parent polysilane. A similar low-frequency absorption was observed for the S-substituted model disilane compound $Ph_2SiH\text{-}Si(STol^p)Ph_2$ (Supporting Information). These are attributed to $\nu_{\text{Si−S}}$.[15,16]

^{13}C DEPT135 NMR also provides evidence for thiolato side-chain incorporation in these modified polymers (Figure 2 and

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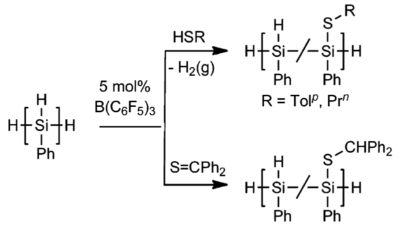
Scheme 1



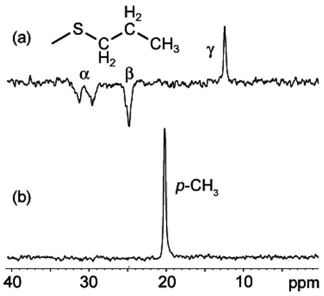


Figure 2. Alkyl region of the 75 MHz ^{13}C DEPT135 NMR for (a) the $-$SPr^n modified polymer and (b) the $-$STol^p modified polymer, in d_6-benzene.

Supporting Information). We see two distinct signals corresponding to the CH$_2$ groups *α* to sulfur in the *n*-propyl side chains (confirmed by an ^{1}H/^{13}C HSQC experiment), which suggests that two unique magnetic environments exist for the SPr^n groups along the modified chain and that the ^{13}C chemical shift difference falls off with distance from the Si$-$S bond. ^{29}Si DEPT90 NMR experiments (using $^1J_{\text{Si}-\text{H}}$ = 188 Hz) confirm the persistence of unsubstituted Ph(H)Si repeat units in the backbone of the modified polymers (broad massif at $-$50 to $-$65 ppm in Figure 3) and also apparently illustrate the presence of two magnetically distinct thiolate-substituted end groups X$-$Si(H)SR, where X = oligomer or polymer chains. These peaks between $-$10 and $-$20 ppm have chemical shifts similar to peaks due to the S-substituted silicons in our model disilanes (Supporting Information) and are absent in the spectrum for the parent poly(phenylsilane). Although long-range polarization transfer experiments (^{29}Si DEPT30, with $^3J_{\text{Si}-\text{H}}$ = 8 Hz corresponding to the four H$_{\text{ortho}}$ protons on each SiPh$_2$ unit) gave signals for the quaternary, S-substituted silicons for samples of our model disilane model compounds, Ph$_2$SiH$-$SiPh$_2$(SR) (Supporting Information), similar experiments using the parent and modified polymer samples (DEPT45 optimized for two H$_{\text{ortho}}$ protons on each SiPh unit) showed no quaternary or tertiary silicon signals, even with variation of the coupling constant and with long acquisition times.

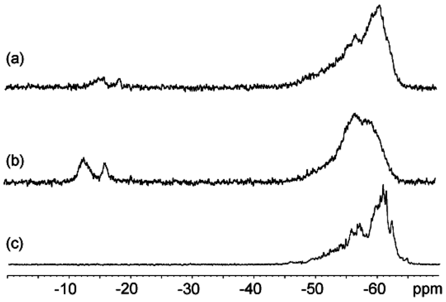


Figure 3. 99 MHz ^{29}Si DEPT90 NMR for (a) the $-$SPr^n modified polymer, (b) the $-$STol^p modified polymer, and (c) the parent poly(phenylsilane), in d_6-benzene.

Addition of B(C$_6$F$_5$)$_3$ to a mixture of poly(phenylsilane) and dark blue S$=$CPh$_2$ in toluene caused an immediate color change to green (Scheme 1, bottom), corresponding to at least partial reduction of the intensely colored thioketone via hydrosilation. As for the dehydrocoupling products described above, the resulting modified polymer was isolated as an off-white solid after trituration of the green reaction residues with pentane. Although its IR spectrum is consistent with partial replacement of the Si$-$H bonds with SR fragments, this derivative proved more difficult to analyze by ^{1}H NMR, since the signal due to the benzylic proton in the thiolato side chains overlaps with that due to the residual Si$-$H bonds. This prevented us from estimating the degree of Si$-$H substitution in the modified polymer. However, the overall broadening of peaks in this region and in the aromatic region is consistent with a polymer structure relatively similar to those obtained for the thiol dehydrocoupling derivatives (Figure 4a). Although very weak,[17] a broad signal for the benzylic carbon from the new side chains can be seen at ~53 ppm in the ^{13}C DEPT135 NMR (Figure 4b). Small, sharp signals in both the ^{1}H and ^{13}C NMR spectra of this polymer correspond to two side products that result from "over-reduction" of the thiobenzophenone in the borane-catalyzed hydrosilation reaction: diphenylmethane and 1,1,2,2-tetraphenylethane. We see these byproducts even when the borane catalyst loading is reduced to 0.5%, at which point the apparent degree of substitution of Si$-$H bonds is very low. Analogous "C$=$O to CH$_2$" reduction chemistry has previously been observed in B(C$_6$F$_5$)$_3$-mediated reactions of tertiary silane Si$-$H bonds with substrates containing carbonyl, alcohol, and ether functionalities.[18] Control reactions of thiobenzophenone with PhSiH$_3$, Ph$_2$SiH$_2$, and HPh$_2$Si$-$SiPh$_2$H in the presence of borane catalyst show that a similar "over-reduction" to diphenylmethane occurs rapidly and quantitatively for the primary and secondary silanes, but not for the crowded tertiary *sym*-disilane (Scheme 2).[19] However, the disilane hydrosilation product **A** does react rapidly with Ph$_2$SiH$_2$ in the presence of borane to give diphenylmethane and the unsymmetric disilathiane **B**, as determined by ^{1}H NMR (eq 1). We conclude that the diphenylmethane observed in samples of the hydrosilation-modified poly(phenylsilane) must be formed via

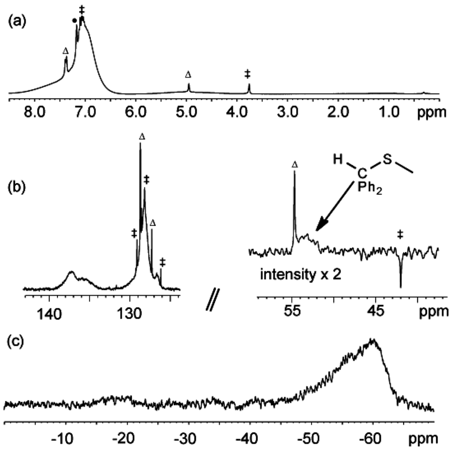
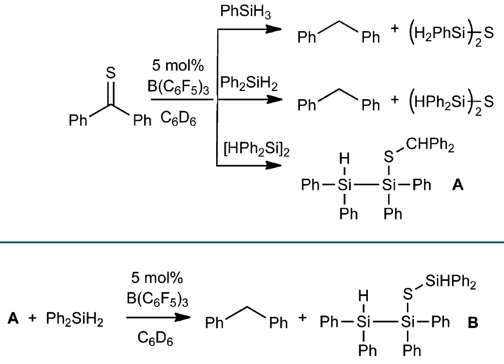


Figure 4. (a) 500 MHz ^{1}H, (b) 75 MHz ^{13}C DEPT135, and (c) 99 MHz ^{29}Si DEPT90 NMR spectra of the $-$SCHPh$_2$ modified polymer in d_6-benzene. The ● denotes residual solvent proton signal, ‡ denotes diphenylmethane, and △ denotes 1,1,2,2-tetraphenylethane.

Scheme 2



[1]

intramolecular "back-biting" reactions of unreacted end groups $-Si(Ph)H_2$ with internal $-Si(Ph)(SCHPh_2)-$. This is consistent with the drastically reduced intensity of signals due to $-Si(Ph)(SCHPh_2)H$ end groups from −10 to −20 ppm in ^{29}Si DEPT90 spectra of samples of the thioketone-derivatized polymer (Figure 4c) and also with light-scattering MW data (vide infra) which are too low to indicate intermolecular reactions leading to cross-linking.

Importantly, we see no evidence for Si−Si bond cleavage reactions occurring during these polymer modifications. GC/MS and ^1H and ^{19}F NMR analysis of the pentane or hexanes washings of the crude polymers showed only $B(C_6F_5)_3$, unreacted sulfur substrate, or, in the case of the hydrosilation reaction, diphenylmethane and 1,1,2,2-tetraphenylethane—no very low MW silanes were detected, even at long GC elution times.[20] MALS-GPC analysis (Table 1 and Supporting Information) shows increased MWs for all three of the modified polymers. Slight increases in polydispersity correspond to increases in intensity at the higher rather than the low MW edge of the traces, which can be attributed to a largely unchanged distribution of polymer backbones that has undergone nonuniform side-chain additions.

Table 1. Molecular Weight Data (in Da) Obtained from Multi-Angle Light-Scattering (MALS) GPC for Multiple Batches of Modified Polymers $H-[SiHPh]_n-[Si(SR)Ph)]_m-H^a$

SR	M_w	M_n	M_w/M_n
$SCH_2CH_2CH_3$	6900 ± 600	4000 ± 300	1.7
$SCH_2CH_2CH_3$	4500 ± 100	2500 ± 200	1.8
$SC_6H_4CH_3$	5400 ± 400	3400 ± 200	1.6
$SC_6H_4CH_3^b$	5000 ± <100	3100 ± <100	1.6
$SCHPh_2$	5100 ± 100	2500 ± 100	2.0
$SCHPh_2$	5700 ± 400	2600 ± 300	2.2

[a] Except where noted, the parent poly(phenylsilane) had M_w/M_n (PDI) = 3500/2200 (1.6). Errors are standard deviations for triplicate runs for each batch. [b] The parent poly(phenylsilane) had M_w/M_n (PDI) = 2600/1700 (1.5).

UV−vis absorptions of the modified polymers in solution show bathochromic shifts relative to λ_{max} ~295 nm, observed for the parent poly(phenylsilane) (Figure 5), consistent with the (probably combined) effects of increased rigidity due to replacement of Si−H groups with larger thiolate side chains and the electronic contributions of the S heteroatoms on the σ-conjugated polysilane backbone.[2b] Similar shifts were reported by Waymouth[7b] and Shankar[7d] for Si−C and Si−O modified poly(phenylsilanes). We have not yet investigated with rigor the photostability of the new polymers but note that spectra of NMR samples that are not protected from ambient light remain unchanged over days to weeks.[21] Also, solid samples stored in the glovebox, again with no protection from ambient light, show no degradation over months.

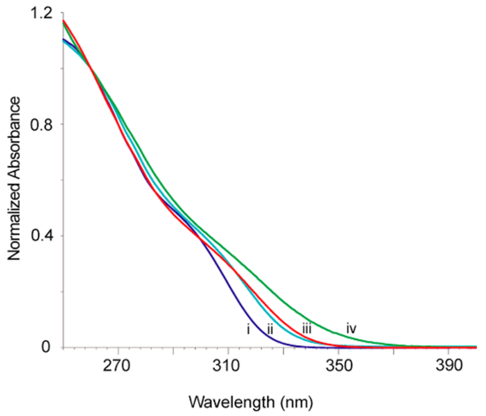


Figure 5. UV−visible absorption spectra of (i) the parent poly(phenylsilane) and the (ii) $-SPr^n$, (iii) $-STol^p$, and (iv) $-SCHPh_2$ modified polymers in dichloromethane (0.1−0.3 mg/mL) at room temperature.

We are currently exploring the substrate scope for heterodehydrocoupling and hydrosilation reactions of poly(phenylsilane) using this mild and selective technique, with a view to introducing a wider range of Si−element bonds including Si−O,[22] Si−C,[23] and Si−N.[24] These results, along with our exploration of the materials properties of the resulting thin films, will be reported in due course.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, and a table giving experimental details and selected spectroscopic and GPC data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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■ REFERENCES

(1) Recent reports include: (a) Klausen, R. S.; Widawsky, J. R.; Steigerwald, M. L.; Venkataraman, L.; Nuckolls, C. *J. Am. Chem. Soc.* **2012**, *134*, 4541. (b) Wang, Q.; Lu, H.; Gai, L.; Chen, W.; Lai, G.; Li, Z. *Dyes Pigm.* **2012**, *94*, 183. (c) Chung, W.; Shibaguchi, H.; Terao, K.; Fujiki, M.; Naito, M. *Macromolecules* **2011**, *44*, 6568. (d) Feigl, A.; Bockholt, A.; Weis, J.; Rieger, B. *Adv. Polym. Sci.* **2011**, *235*, 1. (e) Nemec, H.; Kratochvilova, I.; Kuzel, P.; Sebera, J.; Kochalska, A.; Nozar, J.; Nespurek, S. *Phys. Chem. Chem. Phys.* **2011**, *13*, 2850. (f) Ostapenko, N.; Vodolazkyy, P.; Peckus, D.; Gulbinas, V.; Moiseenko, V.; Surovtseva, N.; Suto, S.; Watanabe, A. *Mol. Cryst. Liq. Cryst.* **2011**, *536*, 41. (g) Semenov, V. V. *Russ. Chem. Rev.* **2011**, *80*, 313. (h) Deepak; Banerjee, N.; Seki, S. *J. Appl. Phys.* **2010**, *107*, 124513/1. (i) Dostie, S.; Aktik, C.; Scarlete, M. *Macromol. Containing Met. Met.-Like Elem.* **2010**, *10*, 205.

(2) (a) Bande, A.; Michl, J. *Chem. Eur. J.* **2009**, *15*, 8504. (b) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.

(3) (a) Hill, M. S. *Struct. Bond.* **2010**, *136*, 189. (b) Chatgilialoglu, C.; Guerrini, A.; Lucarini, M.; Pedulli, G. F.; Carrozza, P.; Da Roit, G.; Borzatta, V.; Lucchini, V. *Organometallics* **1998**, *17*, 2169.

(4) Corey, J. Y. *Adv. Organomet. Chem.* **2004**, *51*, 1.

(5) (a) Marciniec, B. *Comprehensive Handbook on Hydrosilation*; Pergamon Press: Oxford, U.K., 1992. (b) Marciniec, B., *Hydrosilation: A Comprehensive Review on Recent Advances*. Springer: 2008.

(6) Koe, J. *Polym. Int.* **2008**, *58*, 255.

(7) Waymouth prepared functionalized polysilanes by radical-induced halogenation[7a] and hydrosilation reactions[7b] of Si−H bonds in poly(arylsilanes). The latter method (∼10 mol % AIBN @ ≥90° gives 50−90% substitution of Si−H bonds) serves as a benchmark for the variety of polysilane derivatives it has been used to prepare (e.g. refs 7c−e). Harrod[7f] and Woo[7g,h] both reported metallocene-catalyzed dehydropolymerization reactions of arylsilanes in which heterodehydrocoupling of Si−H bonds with added alcohols or ammonia provides one-pot routes to alkoxy- and amino-substituted poly(arylsilanes), and Harrod reported the incorporation of pendant cyclohexyl groups when using cyclohexene as a hydrogen acceptor during the titanocene-mediated dehydropolymerization of phenylsilane.[7i] Tanaka used $AlCl_3$-catalyzed hydrosilation of alkynes and alkenes to modify oligosilanes with Si−H repeat units.[7j] (a) Banovetz, J. P.; Hsiao, Y. L.; Waymouth, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 2540. (b) Hsiao, Y.-L.; Waymouth, R. M. *J. Am. Chem. Soc.* **1994**, *116*, 9779. (c) Beach, J. V.; Loy, D. A.; Hsiao, Y. L.; Waymouth, R. M. *ACS Symp. Ser.* **1995**, *614*, 355. (d) Shankar, R.; Joshi, A. *J. Organomet. Chem.* **2006**, *691*, 3310. (e) Shankar, R.; Shahi, V. *J. Organomet. Chem.* **2008**, *693*, 307. (f) Liu, H. Q.; Harrod, J. F. *Organometallics* **1992**, *11*, 822. (g) Kim, B. H.; Cho, M. S.; Kim, M. A.; Woo, H. G. *J. Organomet. Chem.* **2003**, *685*, 93. (h) Kim, B.-H.; Woo, H.-G. *Adv. Organomet. Chem.* **2005**, *52*, 143. (i) Harrod, J. F. *ACS Symp. Ser.* **1988**, *360*, 89. (j) Kato, N.; Tamura, Y.; Kashiwabara, T.; Sanji, T.; Tanaka, M. *Organometallics* **2010**, *29*, 5274.

(8) Stoichiometric modification of poly(methylphenylsilane) by acetyl chloride/$AlCl_3$ converts Si−Ph to reactive Si−Cl: (a) Tang, H.; Liu, Y.; Huang, B.; Qin, J.; Fuentes-Hernandez, C.; Kippelen, B.; Li, S.; Ye, C. *J. Mater. Chem.* **2005**, *15*, 778. (b) Herzog, U.; West, R. *Macromolecules* **1999**, *32*, 2210. There is some debate over the chemoselectivity of a comparable transformation (Si−Ph to Si−OTf) using triflic acid: (c) Corey, J. Y.; Kraichely, D. M.; Huhmann, J. L.; Braddock-Wilking, J.; Lindeberg, A. *Organometallics* **1995**, *14*, 2704. (d) Uhlig, W. *Prog. Polym. Sci.* **2002**, *27*, 255.

(9) For example, Sacarescu has functionalized Si−H-containing copolymers via platinic acid-catalyzed hydrosilation of alkenes[9a] but notes facile competing chemical degradation at the Si−H-containing repeat units in these polymers.[9b,c] (a) Sacarescu, L.; Ardeleanu, R.; Sacarescu, G.; Simionescu, M. *High Perform. Polym.* **2007**, *19*, 510. (b) Sacarescu, L.; Siokou, A.; Sacarescu, G.; Simionescu, M.; Mangalagiu, I. *Macromolecules* **2008**, *41*, 1019. (c) Simionescu, M.; Sacarescu, L.; Sacarescu, G. *Des. Monomers Polym.* **2012**, *15*, 127. References 8a,b report Si−Si bond cleavage during $AlCl_3$-mediated Si−Ph modification chemistry. The sensitivity of Si−H units in poly(hydrosilanes) to radical cleavage reactions has been described by Chatgilioglu.[3b]

(10) Little or no Si−Si bond cleavage (or diminished MWs) was reported in refs 7b−e,7g,7h, and the modified polysilanes described in refs 7b−e give GPC and UV−vis data consistent with reasonable degrees of polymerization.

(11) (a) Harrison, D. J.; Edwards, D. R.; McDonald, R.; Rosenberg, L. *Dalton Trans.* **2008**, 3401. (b) Harrison, D. J.; McDonald, R.; Rosenberg, L. *Organometallics* **2005**, *24*, 1398. (c) Harrison, D. J. M.Sc. Thesis, University of Victoria, Victoria, British Columbia, 2005.

(12) Piers, W. E.; Marwitz, A. J. V.; Mercier, L. G. *Inorg. Chem.* **2011**, *50*, 12252.

(13) We prepared the parent polymer by zirconocene-mediated dehydrocoupling of phenylsilane,[4] using a slightly modified literature procedure[7b] (see the Supporting Information). This method gives mixtures of linear polysilane and cyclic oligomers.

(14) The breadth of signals in the ^1H NMR spectra have not allowed us to gauge whether the cyclic or linear portions of the polymer are more highly substituted, but we are currently investigating the impact of higher catalyst loadings on the overall degrees of Si−H substitution in the modified polymers. The current reaction conditions (details in the Supporting Information) were those established previously,[11] using catalyst loadings optimized for the modification of *sym*-tetraphenyldisilane, in which the Si−H bonds are quite sterically hindered. The borane catalyst can be used in nonpolar hydrocarbons and dichloromethane but not in strongly coordinating solvents; the solubility of poly(phenylsilane) dictated our choice of toluene here. Control reactions carried out on an NMR scale confirm that no Si−H transformations occur in the absence of catalyst, even with heating up to 70 °C.

(15) These correspond with ν_{Si-S} values previously reported for disilthianes in the gas phase. Drake, J. E.; Glavincevski, B. M.; Hemmings, R. T. *Can. J. Chem.* **1980**, *58*, 2161.

(16) Elemental analyses also confirm the presence of S in these modified polymers (see the Supporting Information).

(17) The difficulty in observing the ^{13}C signal due to the benzylic carbon in the $-SCHPh_2$ polymer can be rationalized on the basis of poor polarization transfer from the single attached proton, relative to the $-CH_3$ in the $-STol^p$ polymer and the α-CH_2 in the $-SPr^n$ polymer, as well as the lower solubility of this polymer in d_6-benzene relative to the other polymers. In addition, we have determined that at least some of the $-SCHPh_2$ side chains in this polymer undergo a side reaction in the presence of the borane catalyst (vide infra).

(18) See ref 12 and: (a) Bajracharya, G. B.; Nogami, T.; Jin, T.; Matsuda, K.; Gevorgyan, V.; Yamamoto, Y. *Synthesis* **2004**, 308. (b) Gevorgyan, V.; Rubin, M.; Benson, S.; Liu, J.-X.; Yamamoto, Y. *J. Org. Chem.* **2000**, *65*, 6179. These references do not, however, report C−C bond coupling of liberated benzylic fragments to give 1,1,2,2-tetraphenylethane, and we do not observe this product in control reactions of the thioketone with discrete mono- and disilanes. We do not yet understand why it forms in the polymer hydrosilation reactions.

(19) This sensitivity of the rates of Si-H activation mediated by $B(C_6F_5)_3$ to increased steric hindrance at silicon is general[11a,c,12] and precludes a possible one-pot synthesis of the modified polymers directly from phenylsilane and S-containing substrates using combined Zr and borane catalysts: the Si−H bonds in phenylsilane react much faster with S-substrates than those in the polymer, which competes with the dehydropolymerization. A sequential, as opposed to simultaneous, one-pot synthesis—i.e. adding borane and S-substrate directly to the already polymerized mixture—is an appealing alternative but also presents challenges, since solvent must be added. In solution, in the presence of Zr catalyst, the linear poly(phenylsilane) chains undergo significant decomposition to cyclic oligomers.[4]

(20) The SPr^n-modified polymer is slightly soluble in these nonpolar organics. ^1H NMR of these washings showed weak signals identical with those for the bulk, isolated polymer.

(21) An exception is the $-SPr^n$-modified polymer, for which NMR samples eventually show small amounts of $HSPr^n$ attributable to the hydrolysis of Si−S bonds by trace moisture.

(22) (a) Parks, D. J.; Piers, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 9440. (b) Blackwell, J. M.; Foster, K. L.; Beck, V. H.; Piers, W. E. *J. Org. Chem.* **1999**, *64*, 4887.

(23) Rubin, M.; Schwier, T.; Gevorgyan, V. *J. Org. Chem.* **2002**, *67*, 1936.

(24) Blackwell, J. M.; Sonmor, E. R.; Scoccitti, T.; Piers, W. E. *Org. Lett.* **2000**, *2*, 3921.