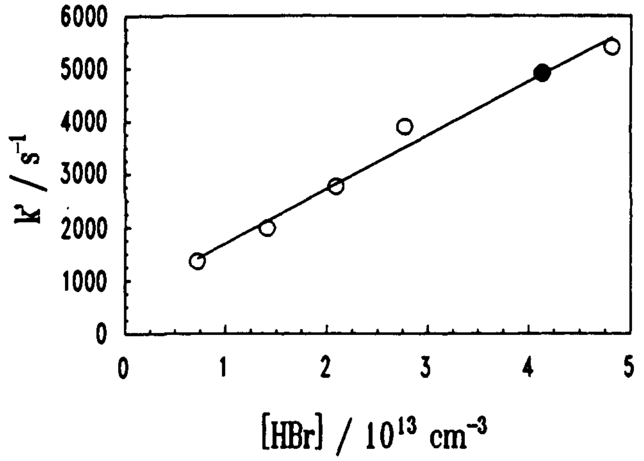

Figure 2. Plot of pseudo-first-order rate constants for formation of Br vs [HBr] at 291 K and 47 mbar. The filled circle corresponds to the data of Figure 1.

Table I. Summary of Kinetic Measurements on $(CH_3)_3Si$ + HBr[a]

P, mbar	τ_{res}, s	F, J	$[(CH_3)_3SiI]$, 10^{14} cm^{-3}	k_1, 10^{-11} cm^3 s^{-1}
45.2	0.7	4.05	3.06	8.5 ± 0.6
47.3	0.8	5.00	3.16	10.5 ± 0.7
47.3	0.8	2.45	3.16	10.1 ± 0.6
46.0	1.0	4.05	4.69	5.8 ± 0.2
46.1	0.6	4.05	3.03	5.7 ± 0.4
45.5	0.5	4.05	1.21	10.2 ± 0.2
32.0	0.5	4.05	2.46	5.2 ± 0.7
31.2	0.5	4.05	2.44	6.0 ± 0.6

[a] Made between 289 and 296 K, with a maximum [HBr] of typically 5×10^{13} cm^{-3}. 1σ statistical precision quoted for k_1.

as a major product. The time dependence of [Br] was interpreted according to the following scheme in addition to reaction 1:

$(CH_3)_3Si \rightarrow$ pseudo-first-order loss by processes which do not generate Br (2)

Br $\rightarrow$ pseudo-first-order loss by diffusion and other slow processes (3)

Other radicals which might be created photolytically and could lead to Br production are H and CH_3, but their reactions with HBr are more than 1 order of magnitude slower than that of $(CH_3)_3Si$.[10,12–14] An alternative product channel for reaction 1, formation of a bromide and atomic H, was found to be negligible in tests using Lyman-α fluorescence detection.[8] As shown in similar experiments involving the reactions of H, alkyl, and thiyl radicals with HBr,[10,12,13,15,16] [Br] is expected to vary as

$$[\mathrm{Br}] = A \exp(-k_3 t) - B \exp(-k' t) \qquad (4)$$

where $k' = k_1[\mathrm{HBr}] + k_2$. We obtained the four parameters of eq 4 from nonlinear least-squares fits to fluorescence decays such as that shown in Figure 1 (the first ≈100 μs are obscured by scattered light from the photolysis flash) and derived k_1 as the slope of a linear plot of k' vs [HBr] as shown in Figure 2. k_3 describes the loss of Br by, e.g., diffusion and a slow reaction with $(CH_3)_3SiI$.[8] k_2 was large, in the range of 500–3000 s^{-1}, and so cannot reflect diffusion alone. Wine and co-workers observed similar rapid alkyl radical disappearance and speculated about roles for impurities such as O_2 or traces of Br_2 or I_2 in their reactor;[10] similar arguments can be applied here. It is also possible that $(CH_3)_3Si$ reacts readily with $(CH_3)_3SiI$.

The k_1 results are summarized in Table I and show no consistent variation with experimental parameters such as pressure P, average gas residence time τ_{res}, flash energy F, and precursor concentration. The mean k_1 is $(7.8 \pm 0.8) \times 10^{-11}$ cm^3 s^{-1} (1σ precision), about twice the rate constant for t-C_4H_9 + HBr of 3×10^{-11} cm^3 s^{-1} at 298 K.[10,14,15] k_{-1} at this temperature is $(8.0 \pm 1.6) \times 10^{-15}$ cm^3 s^{-1} under conditions where the low-lying states of Br were equilibrated, i.e., the Br was essentially all present as $^2P_{3/2}$.[4] Thus we may obtain $K_{eq} = k_1/k_{-1} = 9.75 \times 10^3$. Bearing in mind that detection of product appearance rather than reactant consumption is often more vulnerable to secondary chemistry, we conservatively allow for a factor of 2 inaccuracy in K_{eq}. This yields $\Delta G = -22.8 \pm 1.7$ kJ mol^{-1}. The value of $\Delta S_{298} = -28.6 \pm 2$ J K^{-1} mol^{-1} for reaction 1 is derived from the accurately known entropies of HBr and Br,[17] coupled with the difference in S between $(CH_3)_3Si$ and $(CH_3)_3SiH$ calculated from ab initio data.[4] The uncertain contributions of internal rotors within the silicon species thus largely cancel. This yields $\Delta H_{298} = -31.3$ kJ mol^{-1} $= D_{298}(\mathrm{H{-}Br})$[17] $- D_{298}((CH_3)_3Si{-}H)$, and hence the bond dissociation enthalpy is 398 ± 2 kJ mol^{-1}. The confidence interval allows for errors in K_{eq} and ΔS. This value confirms the previous estimate and the implications for other bond strengths and enthalpies of formation given earlier[4] but eliminates the need for kinetic assumptions and reduces the uncertainty. Methyl substitution significantly increases the Si–H bond strength in silane, and the best estimate of $\Delta H_{f,298}((CH_3)_3Si)$ is 17 ± 4 kJ mol^{-1}, where the main source of uncertainty is now $\Delta H_{f,298}((CH_3)_3SiH)$.[18] These results imply a negative activation energy of about -3 kJ mol^{-1} for k_1, which will be investigated in future work.

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Selective Free-Radical Halogenation of Polyphenylsilane

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Polysilanes constitute a novel class of materials with unique electronic properties.[1] The unusual properties of these polymers are influenced by the polymer conformation, the molecular weight, and the substituents attached to the polymer backbone.[2] Conventional methods of synthesizing these materials are intolerant of many functional groups and offer limited potential for control of stereochemistry or molecular weight.[3,4] In contrast, recently

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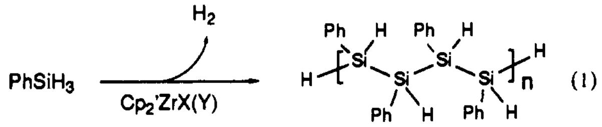
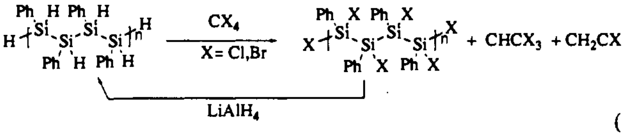
developed[5] transition-metal mediated syntheses present exciting opportunities for the synthesis of polymers of defined structure and functionality. Although the molecular weights of materials prepared with transition-metal catalysts remain modest, catalytic routes offer the potential for preparing polymers of defined tacticity. In addition, polymers obtained from the catalytic polymerization of terminal silanes contain reactive Si–H bonds that can be further functionalized.[6] We have recently reported the stereoselective polymerization of phenylsilane in the presence of zirconocene catalysts.[7] In this communication, we report the remarkably selective free-radical halogenation of these materials to afford a new class of silicon polymers, polyphenylhalosilanes.

Catalytic polymerization of phenylsilane with zirconocene derivatives $Cp'_2ZrX(Y)$ (Cp' = cyclopentadienyl, ethylenebis(indenyl); X = H, Cl, alkyl; Y = Cl, alkyl) yields polyphenylsilane (eq 1).[5-7] Selective chlorination of this material can be carried out with mild halogenating agents such as CCl_4 and CBr_4. Treatment of the polyphenylsilane with CCl_4 at room temperature for 28 h yields a new polymer, characterized as polyphenylchlorosilane (eq 2),[8] along with chloroform and methylene chloride, as determined by GC and ^1H NMR. Analysis of the isolated polymer by IR[9] revealed that greater than 84% of the Si–H bonds had been chlorinated under these conditions. Treatment of polyphenylsilane with CCl_4 for longer periods of time (5 days) increases the chlorination to >95% of the Si–H bonds. Chlorination of a fractionated[7] sample of polyphenylsilane (M_W/M_n = 4665/3611 = 1.29) affords polyphenylchlorosilane of similar molecular weight and molecular weight distribution (M_W/M_n = 4736/2569 = 1.84), indicating that the chlorination reaction is selective for Si–H bonds.[10] Halogenation of polyphenylsilane with CBr_4 affords polyphenylbromosilane.



(1)

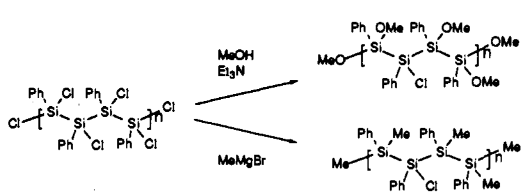


(2)

When monitored by GC or ^1H NMR, the halogenation reaction was observed to be enhanced by light and radical initiators such as $Mn_2(CO)_{10}$ and retarded by the presence of BHT, indicative of a free-radical process. Radical initiators are not required; presumably, light-induced homolysis of Si–Si bonds[1] or photoxidation provides the necessary initiators for the free-radical chain process. Further studies to probe these hypotheses are in progress.

Substitution of the Si–Cl bonds can be carried out with a variety of nucleophiles. Reduction of the chlorosilane polymer with $LiAlH_4$ regenerates polyphenylsilane. While the chlorination appears to be selective for Si–H bonds, reduction of polyphenylchlorosilane with $LiAlH_4$ leads to substantial Si–Si bond cleavage;[11] efforts to completely reduce the fractionated sample of polyphenylchlorosilane (M_W/M_n = 4736/2569 = 1.84) yielded low-molecular-weight oligophenylsilanes (M_W/M_n = 600/192 = 3.12). However, chlorination of a stereoregular sample of polyphenylsilane (M_W = 3004, M_W/M_n = 1.79)[7] followed by reduction under carefully controlled conditions afforded polyphenylsilane (M_W = 2213, M_W/M_n = 1.42) with a ^{29}Si NMR spectrum remarkably similar to the original sample (see supplemental material), suggesting that the free-radical chlorination and subsequent reduction are *stereospecific*.[12,13]

Alcohols can be substituted onto the polymer backbone under mild conditions in the presence of triethylamine (eq 3). In preliminary investigations, up to 56% of the Si–Cl bonds could be substituted with MeOH, as determined by ^1H NMR. Treatment of polyphenylbromosilane (M_W = 1039, M_W/M_n = 2.09) with methanol under identical conditions yields 70% incorporation. Alkylation of polyphenylchlorosilane (M_W = 1718, M_W/M_n = 7.16) with MeMgBr yielded polyphenylmethylsilane with 70% incorporation of methyl groups onto the polymer backbone (M_W = 2947, M_W/M_n = 2.41).[14]



(3)

In conclusion, we report the mild and selective free-radical halogenation of polyphenylsilane to yield a novel class of halogenated polysilanes. These reactions promise to complement existing functionalization techniques for polyphenylsilanes with triflic acid.[15] In addition, the selectivity of this halogenation procedure, combined with the facile substitutional lability of silicon–halogen bonds, promises to lead to a wide variety of new silicon polymers with interesting physical and electronic properties.

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Supplementary Material Available: Experimental details and ^{29}Si NMR spectra (5 pages). Ordering information is given on any current masthead page.

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(8) Treatment of 300 mg of polyphenylsilane (M_W = 3004, M_W/M_n = 1.79); with 11.0 mL of CCl_4 for 65.5 h yields 380 mg of polyphenylchlorosilane as a white, brittle solid. ^1H NMR ($C_2D_2Cl_4$): 6.3–7.7 (broad), 4.0–5.0 ppm (broad). GPC: M_W = 3367, M_W/M_n = 1.96. IR: 3048, 2989, 2100, 1429, 1102, 731, 694 cm^{-1}.

(9) Determination of the percentage of halogenation by IR was carried out by comparing the intensities of the Si–H stretching frequency at 2100 cm^{-1} to the C=C stretching frequencies centered at 1900 cm^{-1}.

(10) Fractionated polyphenylsilane GPC: M_W = 4665, M_n = 3611, M_W/M_n = 1.29. IR: 3064, 2920, 2095, 1425, 1102, 731, 695 cm^{-1}. Polyphenylchlorosilane GPC: M_W = 4736, M_n = 2569, M_W/M_n = 1.84. IR: 3052, 2106, 1425, 1102, 731, 695 cm^{-1}.

(11) Control experiments demonstrated that $LiAlH_4$ will degrade polyphenylsilane.

(12) Chlorination and reduction of an atactic sample of polyphenylsilane (M_W = 1777, M_W/M_n = 2.55) afforded atactic polyphenylsilane (M_W = 1619, M_W/M_n = 2.34) with an NMR spectrum very similar to that of the starting material.

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