Free-Radical Hydrosilylation of Poly(phenylsilane): Synthesis of Functional Polysilanes

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Soluble polysilanes have recently attracted considerable attention due to their unusual electronic and photophysical properties, as well as their potential applications in microlithography,[1] in ceramics,[2] as photoconducting polymers,[3] and as nonlinear optical materials.[4] The unique electronic and photophysical properties of polysilanes are derived from the extensive delocalization of σ-electrons along the silicon backbone and are extremely sensitive to the nature of the substituents attached to the polymer backbone.[5] The electronic behavior of these materials has stimulated considerable effort to develop selective syntheses of polysilanes with well-defined structure.

Polysilanes are generally synthesized by Wurtz coupling of diorganodichlorosilanes with molten sodium in hydrocarbon solvents or toluene.[5] The introduction of functional organic groups into polysilanes by direct polymerization of functionalized monomers is limited by the vigorous conditions employed in the condensation reaction.[6-8] However, some recent success has been achieved in functionalizing polysilanes prepared by Wurtz coupling, particularly for the phenyl-substituted polysilanes.[8-12] One of the appealing characteristics of polysilanes synthesized by the catalytic dehydrogenative coupling of phenylsilane[13-18] is the reactive Si-H functionality in the polymers prepared by this route. While some efforts have been made to substitute the Si-H bonds by catalytic hydrosilylation,[19,20] we have found it difficult to control the selectivity for Si-H bonds vs Si-Si bonds, leading to considerable depolymerization in the presence of transition metal catalysts.

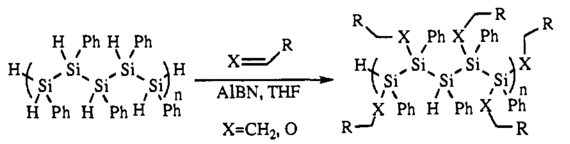
We have recently found that free-radical methods provide a very mild process for selectively substituting the Si-H bonds of poly(phenylsilane). Free-radical chlorination of poly(phenylsilane)[21] with CCl_4 affords poly(chlorophenylsilane), which can be substituted in a subsequent step by mild nucleophiles to give a wide range of functionalized polymers. In this contribution, we report the free-radical hydrosilylation of olefins, aldehydes, and ketones[22-26] as a mild and direct route to a variety of substituted polysilanes. This synthetic strategy has allowed us to investigate both the steric and electronic effects of substituents on the electronic properties of polysilanes.

Table 1. Properties of Functionalized Poly(phenylsilane) $-(PhSiX)_n-$

entry	X	%[a]	M_n[b]	PDI[c]	M_n[d]	DP[e]	λ_{max} (nm)	ϵ[f]
1	H	100	1956	1.66	3647	34	294	2026
2	OC_5H_{11}	80	3905	1.33	4127	24	353	2349
3	C_6H_{13}	84	4084	1.36	5400	31	325	4321
4	$O(c\text{-}C_6H_{10})$	85	2925	1.34	5478	29	343	3562
5	$CH_2(c\text{-}C_6H_{10})$	73	2685	1.40	3414	20	318	3116
6	$(CH_2)_4COOMe$	84	6196	1.42			329	5224
7	$(CH_2)_5OH$	93	2899	1.41			323	3550
8	$(CH_2)_4COOH$	90	3085	1.50			326	4901
9	$(CH_2)_5NMe_2$	86	3967	1.93			326	4115

[a] Determined by ^1H NMR signals of alkyl/aromatic protons. [b] Determined by gel permeation chromatography. [c] PDI = polydispersity index, M_w/M_n, from GPC. [d] Determined by vapor pressure osmometry in toluene, 50 °C. [e] DP = degree of polymerization. [f] Extinction coefficient, in units of $cm^{-1}\ M^{-1}$, in THF.

Catalytic polymerization of phenylsilane with zirconocene derivatives yields poly(phenylsilane).[13-18] Free-radical hydrosilylation can be carried out directly on poly(phenylsilane) in the presence of AIBN [2,2′-azo(bisisobutyronitrile)] by refluxing in neat substrate (such as cyclohexanone or valeraldehyde) or in a solvent (toluene or 2,5-dimethyltetrahydrofuran) for 4–16 h. Suitable substrates include 1-alkenes, ketones, and aldehydes, as shown in Table 1.



(1)

Under these conditions, the degree of substitution ranges from 73% to 93%. The effect of substitution reactions on the number average molecular weight (M_n) of the polymer was investigated by vapor pressure osmometry. The degree of polymerization of 34 silicon atoms was determined for poly(phenylsilane). For entries 2–5, analysis of the substituted polymers revealed only a slight loss in molecular weight following free-radical hydrosilylation.

The selectivity of this free-radical substitution process has allowed us to study the spectroscopic properties of a series of related polysilanes of similar molecular weight. Although there have been numerous studies on the electronic properties of dialkyl, diaryl, and alkyl aryl polysilanes,[5,27,28] few reports exist on the spectroscopic properties of Si-H- or Si-OR-containing polysilanes with degrees of polymerization greater than 5.[29,30] The UV absorption spectrum of phenylsilane oligomers (entry 1) contains a weak transition at 294 nm ($\epsilon_{Si-Si} = 2062\ cm^{-1}\ M^{-1}$, Figure 1a).

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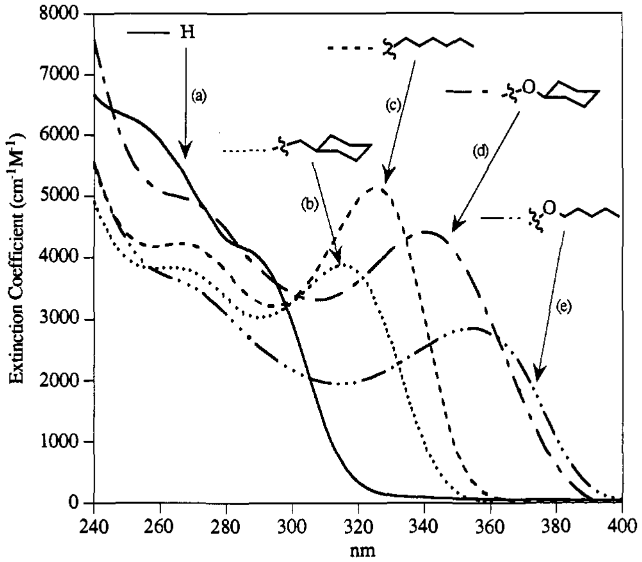

Figure 1. UV spectra of substituted poly(phenylsilane)–$(PhSiX)_n$–: (a) poly(phenylsilane); (b) Poly[(cyclohexylmethylene)phenylsilane]; (c) poly(hexylphenylsilane); (d) poly[(cyclohexyloxy)phenylsilane]; (e) poly[(pentyloxy)phenylsilane].

The position of this absorption maximum is blue-shifted relative to dialkyl-substituted polysilanes of similar molecular weight. Substitution of the Si–H group with a Si–hexyl group results in a red shift of 31 nm and an increase in the extinction coefficient. A similar red shift is observed for other alkyl-substituted derivatives (entries 5–9). We attribute this difference primarily to a difference in conformations for the hydro- and alkyl-substituted phenylsilane polymers. Because the hydrogen substituent is small relative to an alkyl group, it might be expected that a larger number of gauche or eclipsed conformations would be energetically accessible for the hydropolymer, causing the polymer to exist as a tight random coil with few extended trans segments. In contrast, the larger alkyl substituents might be expected to lead to a stiffening in the polymer chain, resulting in a greater population of extended trans segments and thus a red shift in the absorption spectrum.

Even more dramatic changes are observed upon substitution of the hydropolymer with aldehydes and ketones. Replacement of the Si–H substituent with a pentyloxy or cyclohexyloxy substituent results in red shifts of 59 and 49 nm, respectively. In an effort to decouple steric/conformational effects from electronic effects, we prepared a series of structurally related polysilanes where the only difference is the nature of the atom attached to the silicon backbone (entries 2, and 3, 4, and 5). Polysilanes with oxygens attached directly to the silicon backbone absorb at longer wavelengths compared to the structurally similar alkyl-substituted derivatives. A comparison of the hexyl-substituted and the pentyloxy-substituted polysilane shows a difference of 28 nm in the absorption maximum. Similar behavior is seen for the cyclohexylmethylene- and cyclohexyloxy-substituted polysilanes. The difference in the extinction coefficients for the alkyl vs alkoxy polymers is difficult to interpret, but may be due to the different degrees of polymerization.

The differences in the λ_{max} for the alkyl and alkoxy substituents with similar steric demands are likely a result of an electronic perturbation of the silicon backbone by the alkoxy substituents. The lone-pair electrons on the oxygen substituents might be expected to perturb the polymer backbone electronic structure by destabilizing the HOMO more than the LUMO, leading to a decrease of the transition energy.[5,30]

The free-radical hydrosilylation is quite tolerant of a number of polar groups and provides a one-step procedure for introducing functional groups such as hydroxy, amino, or carboxylic acid side chains. The incorporation of hydroxyl, amino, and carboxylic acid functional groups (Table 1, entries 7–9) affords hydrophilic polysilanes which are readily soluble in alcohol.[31] Quaternization of the amino-substituted polysilanes or deprotonation of the carboxylic acid-substituted polysilanes yields water-soluble polysilanes. Thus, this procedure provides considerable synthetic flexibility for the preparation of a wide variety of functionalized polysilanes.

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Supplementary Material Available: Experimental procedures and spectroscopic data for all polymers (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(31) The molecular weights of the hydrophilic polysilanes (entries 7–9) determined by GPC must be interpreted with caution as these materials are likely to adopt unusual conformations due to intramolecular hydrogen bonding, and thus polystyrene will not be an appropriate molecular weight standard.