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Functionalization of Polysilyne Networks for Enhanced Surface Properties

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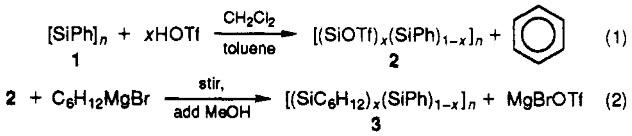
Syntheses of three-dimensional silicon polymer networks, the polysilynes ($[RSi]_n$, R = alkyl), have been recently reported.[1] These new polymers' network backbone confers physical properties which contrast those of one-dimensional or linear silicon backbone polymers, the polysilanes ($[RR'Si]_n$).[2-5] Thus, applications of this class of network polymers may contrast or complement those which have been found for the polysilanes. However, one barrier to full exploitation of the network polymers' novel properties has been the severely reducing reaction conditions needed to synthesize polysilynes[1a-d] which do not allow polymerization of monomers that bear any functional group other than a hydrocarbon. These functional groups are reduced and destroyed during the polymerization, thereby making the synthesis of polysilynes which are functionalized with surface-enhancing or property-altering side chains impossible via this synthetic route. We report here the synthesis of such novel polysilynes, which cannot be formed using the conventional synthesis, via a different route, the assembly of the polymer backbone and its subsequent functionalization with property-altering side chains.

Various studies have established successful dearylation of silicon compounds with hydrohalic acids.[2a] The functionalization of linear polysilane high polymers was also accomplished by this route, using lithium reagents to substitute the former arylsilicon sites.[2b,c] Dephenylation of polysilanes is also reported by reaction with trifluoromethanesulfonic acid (triflic acid, $HOSO_2CF_3$).[6] The triflate anion, OTf^-, was found to be a better leaving group than halides in the substitution of the former arylsilicon sites. We have extended this dearylation and substitution chemistry to network polymer systems and have found it to be an efficient route to the synthesis of functionalized polysilynes.

Our synthetic procedure involves triflic acid dephenylation of poly(phenylsilyne) (1), synthesized by a modification[7] of a previously reported synthesis[1a-d] and subsequent substitution on the polymer backbone by nucleophiles (eqs 1 and 2). In a typical procedure, poly(phenylsilyne) (1, 1.19 g, 11.3 mmol) is dissolved in dichloromethane/toluene (50 mL, 40:60 vol %) under inert atmosphere at 0 °C. Triflic acid (0.30 mL, 3.4 mmol, 30% molar equivalents) is added over 25 min, and the reaction is warmed to room temperature for 1 h after acid addition. This solution is then stirred 2 days at room temperature.[8] As shown in eq 1, this procedure removes the polymer's phenyl substituents as benzene, generating Si-OTf sites on the backbone wherever a phenyl is removed. The triflated polymer, 2, can be isolated at this point as a dark



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[7] An oven-dried 400-mL beaker containing anhydrous THF (250 mL) was placed in a nitrogen atmosphere drybox equipped with a high intensity (475 W, 20 kHz, $^1/_2$-in. tip) ultrasonic immersion horn. The solvent was irradiated at full powder by immersion of the horn, and NaK alloy (9.0 mL, 285 mmol) was added, followed by 3 more min of sonication. A solution of phenyltrichlorosilane (16.0 mL, 100 mmol) in 20 mL of pentane was then added at a controlled rate via an addition funnel over 10 min, followed by further sonication for 10 more min. Phenyl magnesium chloride solution in THF was added to the reaction mixture until a hydrolyzed aliquot tested pH neutral. The reaction mixture was then removed from the drybox to a shielded hood and water was added, after which the organic layer was separated from the aqueous. Addition of methanol to the organic layer precipitated the polymer. The yellow precipitate was collected and purified by reprecipitation with ethanol from a THF solution, then dried overnight under vacuum. Yield = 3.95 g (39%); GPC $\bar{M}_w = 2733$, $P = 1.76$. ^1H NMR δ = 7.0 (br, C_6H_5). $^{13}C\{^1H\}$ NMR δ 134.7 (br, C_6H_5), 137.6 (br, C_6H_5). IR (neat film on KBr, cm^{-1}) 3043 (s), 2924 (w), 2088 (w), 1954 (w), 1887 (w), 1483 (m), 1426 (s), 1187 (w), 1156 (w), 1089 (s), 1067 (m), 1022 (m), 1000 (s), 911 (w), 849 (w), 799 (w), 732 (vs), 693 (vs), 617 (w). Oxygen content (electron microprobe analysis) = 4%.

[8] The reaction time given is a maximum which allows for complete reaction, but which is not always needed.

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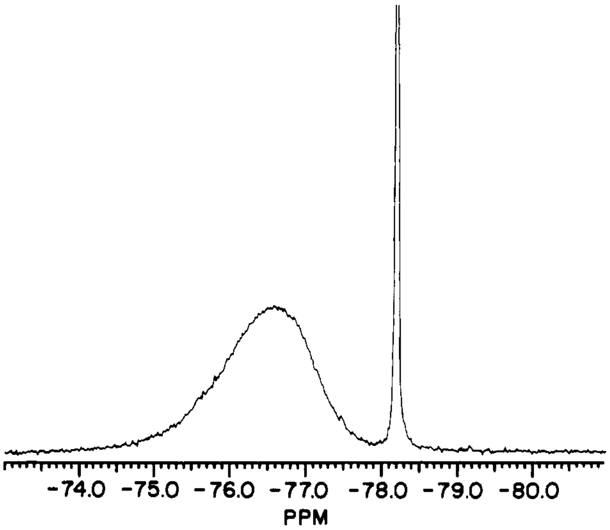

Figure 1. The 188-MHz $^{19}F\{^1H\}$ NMR spectrum of **2** in CD_2Cl_2.[8]

red, extremely air/water-sensitive solid,[9] spectral characterization of which reveals the polymer-bound triflate groups (Figure 1). To functionalize the triflated polymer sites, a nucleophile such as *n*-hexylmagnesium bromide (4.0 mmol, 2.0 M in ether) is added over 10 min to the original solution of **2** at 0 °C, and the reaction mixture is warmed to room temperature one hour after reagent addition. This solution is stirred for 48 h,[8] after which residual triflates are removed by addition of methanol (1.0 mL) and 2,6-di-*tert*-butyl-4-methylpyridine (0.23 g, 1.13 mmol) to trap regenerated triflic acid. The solution is evaporated to dryness, and the new copolysilyne is dissolved in THF, washed with water to remove triflate salts, and precipitated by addition of methanol to remove oligomers. The product is dried under vacuum, producing 0.72 g, 60% yield, of [(70%)poly(phenylsilyne) (30%)-poly(*n*-hexylsilyne)].[10]

The course of the dephenylation and functionalization reactions can be followed by ^1H NMR (Figure 2). Poly(phenylsilyne) displays a broad ^1H resonance centered at 7.0 ppm, which becomes a sharp peak as free benzene is generated by the acid dephenylation. After functionalization with *n*-hexyl groups, the broad but separate ^1H resonances of the phenyl and *n*-hexyl substituents of the produce copolymer can be integrated to assess the completeness of triflate substitution. In this case, integration verifies near-quantitative substitution of 28% of the polymer's phenyl groups, of the 30% attempted. Gel permeation chromatography shows only a twofold increase in molecular weight from starting material ($\bar{M}_w$ = 2733, P = 1.76) to final product ($\bar{M}_w$ = 5378, P = 1.72). Molecular weight increase results from cross-linking of the polymer networks via formation of siloxane links at the reactive triflate sites by traces of oxygen or water (as demonstrated by the increased size of the IR band at 1090 cm^{-1} seen in **3**[10]). A small molecular weight increase indicates that little oxygen has been incorporated into the copolymer in this manner.

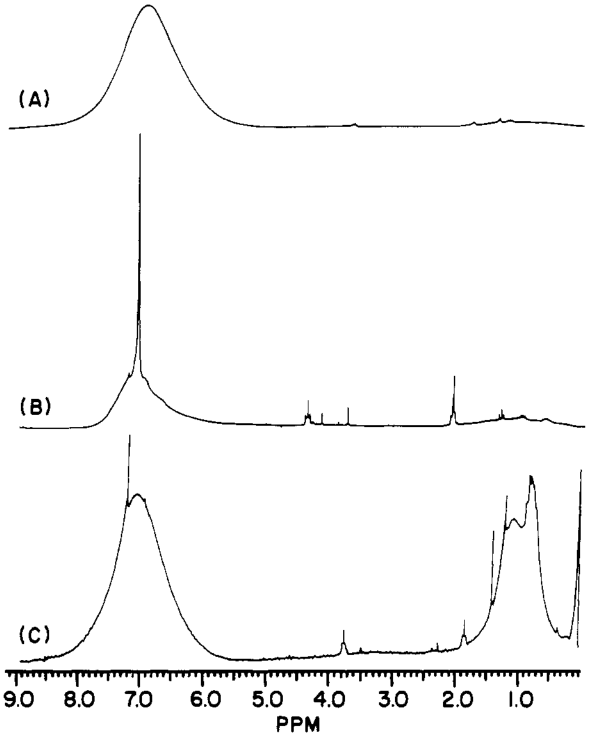

Figure 2. The 200-MHz ^1H NMR spectra of (A) **1**, (B) **2**, and (C) **3** in $CDCl_3$.[7-9] Sharp peaks are solvent impurities which are removed by vacuum.

We have found that the above functionalization procedure for polysilynes required significant modification from the procedure used to functionalize polysilanes.[2a-c,6] The decreased solubility of the network backbone over the linear,[1b] especially when a large percentage of the solubilizing aryl groups have been removed, mandates use of an acid containing a multinuclear acid anion (i.e., one that is bulky is solubilizing) for dephenylation. The extreme rigidity of the network backbone[1b] gives much more resistance to acid degradation than is seen in linear polysilanes,[6b,d] but also slows and inhibits substitution reactions on the backbone. Use of an acid (such as triflic) whose acid anion is an extremely good leaving group is necessary in order to attain efficient substitution and backbone functionalization. Triflation and substitution of polysilynes at levels greater than 70% in one step causes polymer backbone degradation. Triflation at levels approaching 50% becomes increasingly slow and difficult; the triflation procedure generates cationic silyne sites on the backbone, which "holes" can be delocalized via the backbone conjugation. The procedure thus essentially "p-dopes" the silicon clusterlike network. High levels of such positive doping are increasingly unfavorable, and so the triflation reaction slows to inconvenient rates as levels of dephenylation approach 50%.

Our studies on the generality of this functionalization procedure have used alkyl/aryl copolysilyne as starting materials to show that the aryl groups are selectively removed and that these sites are preferentially functionalized.[2a-c,6] This selectivity greatly increases the variety of copolysilynes that can be formed. Functionalization of the backbone with heteroatom-containing groups has also been achieved. For example, the reaction of 1*H*,1*H*-pentafluoropropanol-1 with **2** (in the presence

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[9] Spectral data for **2**: ^1H NMR δ 7.0 (br, C_6H_5), 7.15 (s, C_6H_6). ^{19}F NMR δ = −76.51 (br, $Si[O_3SCF_3]$), −78.21 (br, $Si[O_3SCF_3]_2$). IR (neat film presslocked between KBr plates, cm^{-1}) 3051 (w), 2930 (w), 2109 (w), 1428 (s), 1395 (s), 1265 (s), 1208 (bs, br), 1147 (s), 1092 (s), 1065 (w), 1026 (s), 999 (s), 927 (m), 806 (w), 735 (s), 696 (s), 636 (s).

[10] Spectral data for **3**: ^1H NMR δ = 7.0 (br, C_6H_5), 0.95 (br, C_6H_{13}), 0.79 (br, C_6H_{13}), IR (neat film on KBr, cm^{-1}) 3045 (vs), 2943 (vs), 2924 (vs), 2087 (w), 1953 (w), 1428 (s), 1261 (w), 1188 (w), 1155 (w), 1090 (s), 1066 (m), 1024 (m), 996 (m), 851 (w), 802 (w), 730 (s), 697 (s). Oxygen content (electron microprobe analysis) = 8%.

of a hindered base) produces a surface-modified fluorinated copolysilyne which has been found to be fifty times more sensitive as an ultradeep UV photoresist for 193-nm microlithography than the parent, unfunctionalized polymers.[1e,f] *n*-Butoxy and graft-polyether copolysilynes have also been synthesized from reaction of *n*-butanol or 1,2-propylene oxide (respectively) with **2**. This functionalization method can be extended to other types of property-altering side chains to give a wide variety of new polysilynes, which systems we are continuing to explore.

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