where $\phi_C(x)$ is the preassigned wall profile, defined by eq 2-17. We also have, from the definitions of $\omega_A(x)$ and $\omega_B(x)$

$$\omega_B(x) = \omega_A(x) - g\phi_C(x)[\phi_B(x) - \phi_A(x)] - [\omega_A(\infty) - \omega_B(\infty)] - (\chi_{AC} - \chi_{BC})\phi_C(x) - \chi_{AB}[\phi_B(x) - \phi_A(x) + \phi_A(\infty) - \phi_B(\infty)] \quad \text{(A-6)}$$

Next we solve eq A-1 for polymer B using eq A-5 and A-6 to get the estimates $q'_B(x,t)$, $\phi'_B(x)$. At this point it is convenient to define

$$\frac{\Delta\eta(x)}{\rho_0} = \tfrac{1}{2}\{\omega_A(x) - \omega_A(\infty) + \omega_B(x) - \omega_B(\infty) + (\chi_{AB} - \chi_{AC} - \chi_{BC})\phi_C(x) + g\phi_C(x)[\phi_A(x) + \phi'_B(x)]\} \quad \text{(A-7)}$$

and

$$\phi'_A(x) = 1 - \phi_C(x) - \phi'_B(x) \quad \text{(A-8)}$$

Then we use the quantities $\Delta\eta(x)/\rho_0$, $\phi_A(x)$, $\phi'_B(x)$ in eq 2-27 to obtain $\omega'_A(x)$. It follows, after some algebra, that

$$\omega'_A(x) - \omega_A(x) = \left(\chi_{AB} + \frac{g\phi_C}{2}\right)(\phi'_B - \phi_B) \quad \text{(A-9)}$$

so if $\omega'_A(x) \rightarrow \omega_A(x)$, this implies that $\phi'_B(x) \rightarrow \phi_B(x)$ and $\phi'_A(x) \rightarrow \phi_A(x)$. We want $\omega'_A(x) - \omega_A(x)$ to vanish for all x, but it is sufficient to use $x = x(i)$. This difference, computed at $x = x(i)$, is a functional vector depending on the independent vector $\omega_A(x)$. Note that $\omega'_A(x)$, a vector derived from $\omega_A(x)$, is *not* the next guess for $\omega_A(x)$. The next estimate of $\omega_A(x)$ (to get $\omega'_A(x)$ to converge to $\omega_A(x)$) requires a procedure to solve a nonlinear system of (vector) equations in an unknown vector $[\omega_A(x)]$. For our problem we use the generalized secant method.[10]

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Ultrasound-Mediated Reductive Condensation Synthesis of Silicon–Silicon Bonded Network Polymers

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ABSTRACT: The synthesis of the first poly(alkylsilynes), $(RSi)_n$, a new class of silicon–silicon bonded network materials, has been accomplished by using high-intensity ultrasound to mediate a "virtually homogeneous" reduction of alkylsilicon trichlorides with liquid NaK alloy emulsions. This procedure provides good control over reaction kinetics and stoichiometry by promoting instantaneous initiation and quantitative reaction of the reductant under mild conditions and prevents the premature separation of incompletely reduced polymer. The new polymers $(RSi)_n$ (with R = alkyl > two carbons and $n < 1000$) remain soluble in nonpolar organic solvents, from which they can readily be cast into transparent yellow amorphous films. All chemical and spectroscopic data indicate that polysilynes are constructed primarily of sp^3-hybridized alkylsilicon units assembled into irregular networks that exhibit extensive Si–Si σ-delocalization.

Introduction

Polysilanes, linear polymers possessing an all silicon-silicon bonded backbone, have recently been shown to exhibit a variety of interesting properties and applications that have stimulated extensive research efforts.[1-7] The first example of these materials, poly(dimethylsilane), was described by Burkhard in 1949 as an intractable white powder[3] but received little attention until 1975, when Yajima reported that it could be converted to fibers of β-SiC.[4] The development that accelerated the pace of polysilane research to its current state was the report by West and co-workers of a soluble polysilane, a 1:1 copolymer of dimethylsilane and phenylmethylsilane.[5] While formally analogous to saturated polyolefins, polysilanes typically exhibit an intense near-UV absorption, the position of which shifts with changes in molecular weight and in response to factors affecting the conformation of the polymer backbone.[6] Both the electronic spectra and photochemistry of polysilanes are now generally interpreted by invoking the delocalization of both Si–Si bonding and close-lying antibonding states along the polymer backbone.[1h] Upon irradiation, efficient photofragmentation occurs with extrusion of both silylenes (R_2Si:) and cyclic oligomers, a property which has led to their evaluation as positive photoresists for microelectronics.[7] The intrinsically high silicon content of these polymers is an additional advantage in this application since the unexposed polymer may be converted into SiO_2 by oxygen ion etching.

Although linear polysilanes bearing an impressive diversity of alkyl, aryl, and even trimethylsilyl substituents[8] have now been prepared and investigated, there has been little progress toward the preparation and characterization of monoalkyl silicon polymers, $(RSi)_n$.[9] By direct analogy to carbon-based polymers, materials with a 1:1 alkyl to silicon ratio could adopt either discrete aromatic structures or take the form of linear conjugated polymers analogous to polyacetylenes. Alternatively, and more consistent with the decreased tendency of silicon toward π-bonding, a network structure with no carbon analogue may be adopted. In either case, such materials, viewed as the halfway point between polysilanes and silicon, should exhibit an intriguing array of physical properties.

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In a recent communication[10] we described a new sonochemical procedure for the synthesis of the first such polymer, $(n\text{-}C_6H_{13}Si)_n$, for which we proposed the name "poly(*n*-hexylsilyne)". We now describe in detail the synthesis of this and related poly(alkylsilynes) and evaluate the effect of a variety of synthetic variables on the properties of the resulting polymer.

Experimental Section

All syntheses were done in an inert atmosphere glovebox equipped with a 375-W, 20-kHz ultrasonic immersion horn.[11] Solvents used in the syntheses were Aldrich anhydrous grade. Liquid 1:1 mole ratio NaK alloy was prepared in the glovebox by adding solid potassium to an equimolar amount of molten sodium. Alkyltrichlorosilanes, phenylmethyldichlorosilane, and dihexyldichlorosilane (Silar) and Grignard and lithium reagents (Aldrich) were obtained from commercial sources and used as received. Solution NMR spectra were recorded at room temperature on saturated benzene-d_6 solutions with a Bruker AM-360 MHz spectrometer (90.56 MHz for ^{13}C; 71.55 MHz for ^{29}Si). Solution ^{29}Si chemical shifts were referenced to external hexamethyldisiloxane (7.22 ppm) in benzene-d_6 solution. The solid-state magic angle spinning (MAS) spectra were recorded on a Varian XL-200 spectrometer (50.31 MHz for ^{13}C; 39.75 MHz for ^{29}Si) employing a Doty Scientific MAS probe. Samples were observed in Al_2O_3 rotors at spinning rates of 2.5–4.0 kHz with and without cross-polarization (CP) and with high-power proton dipolar decoupling (DD) of ca. 10 G. Between 250 and 1000 scans were accumulated for each solid-state spectrum. Referencing the carbon spectra to the TMS scale was accomplished by setting the methyl resonance of poly(*n*-hexylsilyne) to 14.5 ppm.[2b] The silicon spectra were referenced to external poly(di-*n*-hexylsilane) at −25.00 ppm vs TMS.[2b] Electronic spectra were measured over the range 190–820 nm on a Hewlett-Packard 8452 UV–vis diode array spectrometer. Infrared spectra were recorded on a Nicolet 5-DX FTIR instrument. Gel permeation chromatography of polysilynes was carried out on THF solutions, filtered through a 0.45-μm filter and protected from light. A Waters Associates Model 244 liquid chromatograph with a μ-Styragel column equipped with both UV (254 nm) and refractive index detectors was used. Gel permeation chromatography of polysilanes was done by Scientific Polymer Products, Ontario, NY, using a Perkin-Elmer Series 10/LC25 R1 liquid chromatograph. All molecular weights are reported versus polystyrene standards. Mass spectra were determined on a HP-5985B quadrupole mass spectrometer by using a high-temperature probe and a heating rate of 30 °C/min. Elemental analyses were obtained from Analytische Laboratorien, Engelskirchen, West Germany. X-ray fluorescence was done on a home-built instrument equipped with a Cr tube and a Princeton Gamma Tech detector and computer. ESR spectra were measured on a modified Varian Model 4502 EPR spectrometer.

Poly(di-*n*-hexylsilane) (1). Method A. NaK alloy (6.21 g, 200 mequiv) in 100 mL of toluene was ultrasonically irradiated at full power for 1 min, forming a blue-green emulsion. This emulsion was added dropwise over approximately 3 min to a stirred solution of dihexyldichlorosilane (26.9 g, 100 mmol) in 100 mL of toluene. The purple reaction mixture was then stirred overnight at room temperature, after which it was brought out of the drybox, and 200 mL of methanol was added. The precipitated polymer (6.60 g, 33%) was collected by filtration, and gel permeation chromatography was done on the crude product. This product consisted of a high molecular weight fraction ($\bar{M}_w = 1.4 \times 10^6$, $P = 1.08$, 19% by area) and an oligomeric fraction ($\bar{M}_w = 690$, $P = 1.15$, 81% by area). The high polymer can be separated from oligomers by reprecipitation from 2-propanol and was identified as poly(di-*n*-hexylsilane) (1) by its electronic spectrum:[1a] UV–vis λ_{max} = 320 nm.

Method B. A solution of dihexyldichlorosilane (26.9 g, 100 mmol) in 200 mL of toluene was ultrasonically irradiated as NaK alloy (6.21 g, 200 mequiv) was added dropwise over 5 min. Sonication was continued for 20 min after the last addition of NaK. The reaction mixture was allowed to stir at room temperature overnight, after which it was brought out of the drybox, and 200 mL of methanol was added. The reaction was filtered, and the precipitated 1 (4.44 g, 24%) was analyzed by GPC. The crude product consisted of a high molecular weight fraction ($\bar{M}_w = 1.25 \times 10^6$, $P = 1.16$, 15% by area) and an oligomeric fraction ($\bar{M}_w = 690$, $P = 1.13$, 85% by area). The high polymer can be separated from oligomers by reprecipitation from 2-propanol: UV–vis λ_{max} = 320 nm.

Poly(phenylmethylsilane). Method A. NaK alloy (6.21 g, 200 mequiv) in 100 mL of toluene was ultrasonically irradiated at full power for 1 min, forming a blue-green emulsion. This emulsion was added dropwise over approximately 3 min to a stirred solution of phenylmethyldichlorosilane (19.1 g, 100 mmol) in 100 mL of toluene. The purple reaction mixture was then stirred overnight at room temperature, after which it was brought out of the drybox, and 200 mL of methanol was added. A vigorous reaction indicated that much NaK remained unreacted, and no solid product could be isolated by this procedure.

Method B. A solution of phenylmethyldichlorosilane (19.1 g, 100 mmol) in 200 mL of toluene was ultrasonically irradiated as NaK alloy (6.21 g, 200 mequiv) was added dropwise over 5 min. Sonication was continued for 20 min after the last addition of NaK. The reaction mixture was allowed to stir at room temperature overnight, after which it was brought out of the drybox, and 200 mL of methanol was added. The reaction mixture was filtered, and the precipitated polymer (4.30 g, 36%) was analyzed by GPC. The product consisted of one low molecular weight fraction: $\bar{M}_w = 1.2 \times 10^3$; $P = 1.58$; UV–vis λ_{max} = 268, 332 nm.

Effect of Ultrasound on 1. A 200-mg portion of 1, made by method A above, with $\bar{M}_w = 1.5 \times 10^6$, was dissolved in 200 mL of toluene and ultrasonically irradiated for 15 min. The solution was evaporated to dryness, and gel permeation chromatography indicated $\bar{M}_w = 1.32 \times 10^5$ for the solid residue.

Poly(*n*-hexylsilyne) (2). NaK alloy (8.86 g, 285 mequiv) was added dropwise directly beneath the tip of the activated sonication horn immersed in a solution of $n\text{-}C_6H_{13}SiCl_3$ (21.96 g, 100 mmol) in 200 mL of pentane. After the addition was complete, ultrasonic irradiation was continued until the reaction mixture was thick and viscous (approximately 5 min). THF (200 mL) was then added, and ultrasonic irradiation was continued for an additional 5 min. A 1.20 M solution of *n*-hexylmagnesium bromide in ethyl ether was added until a hydrolyzed aliquot of the solution tested at neutral pH (approximately 12 mL required). The resulting mixture was removed from the drybox and carefully poured into 200 mL of water[12] under a stream of inert gas. The resulting yellow precipitate was quickly removed from the aqueous phase,[13] redissolved in THF, and precipitated sequentially from water, methanol, and ethanol to give 3.7 g (33%) of poly(*n*-hexylsilyne) (2) as a yellow hexane-soluble powder: ^1H NMR δ 0.95 (br), 1.49 (br); $^{13}C\,\{^1H\}$ NMR δ 14.39 (CH_3), 23.15 (C_5), 30.77 (C_2), 32.22 (C_4), 34.84 (C_3), C_1 broad and unresolved; $^{29}Si\,\{^1H\}$ NMR δ −57; IR (neat film on KBr, cm^{-1}) 2957 (vs), 2919 (vs), 2874 (vs), 2852 (vs), 1466 (s), 1458 (s), 1419 (w), 1379 (m), 1340 (w), 1293 (w), 1249 (w), 1165 (m), 1098 (s), 1042 (m), 1032 (m), 997 (m), 950 (s), 889 (w), 839 (w), 760 (w), 669 (vs); UV–vis (hexanes, 4.0 mM in Si) onset at 450 nm, increasing gradually in intensity with decreasing wavelength, ϵ at 200 nm = 29 000 per Si; mass spectrum (350 °C) *m/e* 84 [C_6H_{12}], 69 [C_5H_9], 56 [C_4H_8], 41 [C_3H_5]. Anal. Calcd for $C_6H_{13}Si$: C, 63.63; H, 11.57; Si, 24.8. Found: C, 63.38; H, 11.25; Si, 24.9.

Poly(*n*-butylsilyne) (3). *n*-Butyltrichlorosilane (19.16 g, 100 mmol) was reduced with NaK alloy (8.86 g, 285 mequiv) following the same procedure that was used to prepare 2. *n*-Butyllithium (2.7 M in hexane, approximately 0.5 mL) was used to titrate the reaction mixture to neutrality, and purification was carried out as described for 2. This procedure gave 2.7 g (32%) of poly(*n*-butylsilyne) (3) as a yellow powder: ^1H NMR δ 1.63 (br), 1.10 (br); $^{13}C\,\{^1H\}$ NMR δ 14.03 (CH_3), 27.8 (C_3), 32.96 (C_2), C_1 broad and unresolved; $^{29}Si\,\{^1H\}$ NMR δ −56; IR (neat film on KBr, cm^{-1}) 2960 (vs), 2922 (vs), 2873 (vs), 2856 (vs), 1463 (vs), 1408 (m), 1377 (s), 1339 (m), 1290 (w), 1270 (w), 1195 (sh), 1174 (m), 1079 (s), 1050 (m), 1015 (s), 1001 (s), 963 (m), 865 (s), 848 (w), 775 (w), 747 (w), 671 (vs); UV–vis (hexanes, 4.0 mM in Si) onset at 450 nm, ϵ at 200 nm = 35 000 per Si; mass spectrum (350 °C) *m/e* 56 [C_4H_8], 41 [C_3H_5], 27 [C_2H_3]. Anal. Calcd for C_4H_7Si: C, 56.39; H, 10.65; Si, 33.0. Found: C, 55.96; H, 10.33; Si, 32.6.

Poly(*n*-propylsilyne) (4a, 4b). *n*-Propyltrichlorosilane (17.75 g, 100 mmol) was reduced with NaK alloy (8.86 g, 285 mequiv) by using a procedure similar to that used for 1. A solution of

Table I
Effects of Varying Monomer/Reductant Stoichiometry on Poly(*n*-butylsilyne)[a]

$$(n\text{-butyl})\mathrm{SiCl_3} + x\mathrm{NaK} \xrightarrow[\text{sonication}]{\text{pentane/THF}} \text{poly}(n\text{-butylsilyne})$$

	$\bar{M}_w$ (GPC		
NaK, equiv	crude	purified	properties
2.40 (80%)	8400	11000	viscous yellow oil
2.85 (95%)	19000	21000	soluble yellow powder
3.00 (100%)	20000	27000	yellow powder, solubility decreases with time
3.60 (120%)	1000	none	colorless oil, contains Si–H

[a] See details in Experimental Section.

propylmagnesium chloride (2.0 M in diethyl ether) was used to titrate the reaction mixture until a hydrolyzed aliquot tested pH 7. The reaction mixture was brought out of the drybox and poured into 200 mL of water under a stream of inert gas. The precipitated yellow material was extracted with 400 mL of THF, and the solution was filtered and poured into 400 mL of methanol. The precipitated polymer was stirred in 400 mL of hexane for 0.5 h, and the mixture was filtered, thereby separating a hexane-insoluble fraction of poly(*n*-propylsilyne) **4a** (approximately 1.28 g, 18%). X-ray fluorescence of **4a** showed between 3% and 4% Cl. The remaining hexane solution was evaporated to dryness, redissolved in THF, and precipitated sequentially with methanol and ethanol in the manner described for **2**. This procedure gave 1.2 g (17%) of hexane-soluble poly(*n*-propylsilyne) **4b**. X-ray fluorescence of **4b** showed <0.1% Cl. **4b**: ^{1}H NMR δ 1.11 (br), 1.23 (br), 1.73 (br); ^{13}C {^{1}H} NMR δ 19.16 (CH$_3$), 24.15 (C$_2$), C$_1$ broad and unresolved; ^{29}Si {^{1}H} NMR δ −56; IR (neat film on KBr, cm^{-1}) 2965 (vs), 2920 (vs), 2860 (vs), 1463 (s), 1411 (w), 1377 (s), 1319 (w), 1210 (w), 1185 (w), 1110 (s), 1061 (s), 1026 (m), 987 (m), 891 (w), 792 (w), 721 (w), 671 (s); UV-vis (hexane, 4.0 mM in Si) onset at 450 nm, ϵ at 200 nm = 28000 per Si; mass spectrum (350 °C) *m/e* 42 [C$_3$H$_6$], 27 [C$_2$H$_3$].

Effect of NaK/Monomer Stoichiometry on Polysilynes. A. *n*-Butyltrichlorosilane (19.16 g, 100 mmol) was reduced with 80% of the stoichiometric amount of NaK (7.45 g, 240 mequiv) following the standard procedure given for **2**. The reaction mixture was titrated with an ether solution of methyllithium until a hydrolyzed aliquot tested pH neutral. The reaction was then quenched with water, and the organic phase was divided into two equal portions. One half was evaporated to dryness, and the solid residue was analyzed by gel permeation chromatography. The other portion was precipitated sequentially with methanol and ethanol, and GPC analysis was performed on the purified polymer. Molecular weights obtained are shown in Table I.

B. The same procedure was used to reduce *n*-butyltrichlorosilane (19.16 g, 100 mmol) with 95% of the stoichiometric amount of NaK (8.86 g, 285 mequiv). A solution of methyllithium in ether was used to titrate the solution to neutrality. Workup as above was done on the two halves of the organic phase of the quenched reaction mixture, and GPC analyses were obtained on the crude and purified polymers (Table I).

C. A similar procedure was used to reduce *n*-butyltrichlorosilane (19.16 g, 100 mmol) with NaK (approximately 9.32 g, 300 mequiv) until a hydrolyzed aliquot of the reaction mixture had reached pH 7. Workup was performed as above, and GPC analyses were obtained on both the crude reaction products and the purified polymer (Table I).

D. *n*-Butyltrichlorosilane (19.16 g, 100 mmol) was reduced with 120% of the stoichiometric amount of NaK (11.2 g, 360 equiv) by using the above procedure. The reaction mixture was then brought out of the drybox, titrated to neutrality with glacial acetic acid under a stream of inert gas, and quenched with water. A GPC analysis was obtained on the crude reaction products (Table I), but solid polymer could not be precipitated from methanol on attempted workup: ^{1}H NMR δ 0.98, 1.50, 1.72 (br, C$_4$H$_9$, 27 H), 3.96, 4.25, 5.08 (br, Si–H, 1 H); IR (neat film on KBr, cm^{-1}) 2066 (s, Si–H).

Solvent Effect on Polysilyne Synthesis. A. NaK alloy (8.86 g, 285 mequiv) was added dropwise beneath the tip of the activated immersion horn to a solution of *n*-butyltrichlorosilane (19.16 g, 100 mmol) in pentane. Sonication was continued for 10 min after the last addition of NaK. The reaction was stirred for 1 h and then titrated to neutrality by the addition of a 1.05 M hexane solution of *n*-butyllithium (approximately 15 mL), after which the reaction mixture was stirred for 30 min. The reaction was then brought out of the drybox and quenched with water, and the polymer was purified in the usual manner. X-ray fluorescence analysis of the poly(*n*-butylsilyne) so obtained showed approximately 2% Cl.

B. The above procedure was repeated using *n*-hexyltrichlorosilane (21.96 g, 100 mmol). No purified polymer was obtained after workup; a viscous orange oil partially soluble in alcohols was the only isolable product.

NaK Alloy Reduction of *n*-Hexyltrichlorosilane without Ultrasound. NaK alloy (8.86 g, 285 mequiv) was added dropwise to a vigorously stirred solution of *n*-C$_6$H$_{13}$SiCl$_3$ (21.96 g, 100 mmol) in 200 mL of pentane. After the addition was complete, THF (200 mL) was added, and stirring was continued for 1 h. The reaction mixture was titrated to neutrality and worked up in the manner described for **2**. IR spectra of the polymeric product so obtained showed strong Si–H and Si–O–Si bands (Figure 1).

Results/Discussion

Synthesis of Polysilanes. Established synthetic approaches to high molecular weight linear polysilanes have all involved minor variations of the reductive condensation of a diorganosilicon dichloride with sodium dispersion in high-boiling hydrocarbon solvents.[1,7] Such reactions typically yield polymer with a complex polymodal distribution of molecular weights often attributed to heterogenous surface-controlled kinetics. Even large variations in molecular weight distribution, caused by changes in solvent polarity, have been rationalized to result from the differing degrees to which the sodium surface is covered with growing polymer and salt.[7] However, Matyjaszewski and co-workers have reported that poly(phenylmethylsilane) may be synthesized at lower temperatures by using ultrasound to regenerate the surface of the solid sodium reductant during the polymerization. This procedure gave high molecular weight poly(phenylmethylsilane) with reduced polydispersity[14] but did not produce high molecular weight dialkylpolysilanes.

As an alternative to conventional heterogeneous reductive condensation syntheses, we began exploring the synthetic utility of sonochemically generated liquid Na/K alloy–hydrocarbon emulsions. In this technique, the two immiscible liquids, NaK alloy and an organic solvent, are emulsified by ultrasonic irradiation with a high-intensity immersion horn. Unlike sonicated solid sodium dispersions produced by the action of ultrasound on solid reductants, the sonochemically emulsified NaK alloy may exhibit reactivity approaching that of a homogeneous reductant.[15]

The utility of this procedure was first evaluated for the reductive condensation synthesis of two prototypical linear polysilanes, poly(di-*n*-hexylsilane) and poly(phenylmethylsilane). Synthesis of each polymer was attempted both by the addition of preformed Na/K alloy emulsions without sonication of the reaction mixture (method A) and by the addition of the liquid alloy to ultrasonically irradiated solutions of the dichlorosilane and growing polymer (method B). Reactions between liquid NaK alloy and dihexyldichlorosilane conducted in both fashions appeared complete (as judged by the absence of hydrogen evolution on workup) without heating after stirring overnight, while solid poly(phenylmethylsilane) was obtained only by method B or by refluxing the preformed emulsion with the phenylmethyldichlorosilane.

The results of these syntheses contrast those obtained by Matyjaszewski and co-workers using solid reductant and lower intensity ultrasound: with both methods A and B, the dialkyl monomer was polymerized to high molecular weight, monodisperse product, but no high polymer was obtained from the phenylmethyldichlorosilane monomer. The greater homogeneity and reducing power of the NaK emulsion over solid sodium dispersion may allow more efficient reduction and polymerization of the dialkyl monomer, while promoting greater degradation of the more easily reduced poly(phenylmethylsilane). While both methods A and B appear to provide more rapid approaches to poly(dialkylsilanes) than do conventional, more heterogeneous procedures, it must be noted that in both cases it was found necessary to stir the final solution overnight before workup to avoid isolating primarily oligomeric material. Ultrasonic irradiation itself degrades high molecular weight polysilanes: when the high molecular weight component of the poly(di-*n*-hexylsilane) product was isolated and sonicated for the same period of time as in method B in toluene, its $\bar{M}_w$ dropped 1 order of magnitude, from 1.5×10^6 to 1.3×10^5. However, given sufficient "set" time, high polymers were obtained in comparable yields without the polymodal molecular weight distributions reported from conventional syntheses.[1,7] The sonochemical emulsion procedure offers another advantage over conventional syntheses in that the reaction of emulsified Na/K is essentially instantaneous and therefore effectively controlled by the addition rate. This greatly reduces the hazard of explosive initiation associated with the accumulation of passivated reductant.

Synthesis of Poly(alkylsilynes). There are a number of complications associated with the extension of heterogeneous reductive condensation reactions to alkyltrichlorosilanes, many of which (in parallel to the history of polysilanes) are ameliorated by the use of monomers containing alkyl groups other than methyl. Thus, to our knowledge the only explicit mention of such a reaction involved the reduction of methyltrichlorosilane in THF with sodium naphthalide to give an intractable solid product.[9a,b]

The use of sonochemically generated NaK emulsions in hydrocarbon solvents greatly facilitated the synthesis of the first alkyl silicon network polymers, the "poly(alkylsilynes)", $(SiR)_n$. By preventing the passivation of the reductant (NaK) with salt and growing polymer, sonication allows the reductive condensations of alkyltrichlorosilanes to be initiated in inert, saturated hydrocarbon solvents, thereby preventing the complications and side reactions often associated with ethereal solvents and electron-transfer reagents.[9a] Thus while THF was found to be essential to effect complete reduction and solvation of polymeric intermediates, it was added only after sufficient sonication of the monomer with NaK alloy alkane emulsions to ensure that all of the trichlorosilane had reacted.

The physical properties of the poly(alkylsilynes) were found to be highly dependent on the reaction stoichiometry used in their synthesis. As summarized in Table I, when *n*-butyltrichlorosilane was condensed with only 2.4 equiv of NaK (with subsequent alkylation of the remaining Si–Cl bonds), the resulting polymer was a viscous yellow oil with a mean molecular weight of only 8400. Poly(*n*-butylsilyne) samples obtained by using 2.85 equiv (95% reduction) and 3.0 equiv of NaK (100%) were isolated as yellow powders displaying higher molecular weights (19 000–20 000), though the polymer obtained with 3.0 equiv was less stable (vide infra). Finally, by use of 3.6 equiv (a 20% excess) of NaK alloy, a colorless oil was obtained, the IR spectrum of which contained a strong Si–H band. Overreduction apparently resulted in depolymerization, giving oligomeric silyl anions which were protonated to silyl hydrides upon workup.

Although using the full 3 equiv of NaK alloy in the reductive condensation does give high polymer, the solubility of the material so obtained decreases with time, possibly due to hydrolysis of residual silicon–chloride bonds or cross-linking of Si–OH and/or Si–H functionalities. This difficulty is circumvented by using only 95% of the required 3 equiv of NaK alloy to effect the reductive condensation and then "capping" the remaining silicon–chloride bonds with a Grignard or lithium reagent. The reaction mixture is titrated with an appropriate alkylating agent (i.e., *n*-hexylmagnesium bromide for poly(*n*-hexylsilyne), etc.) until a hydrolyzed aliquot of the mixture tests at neutral pH, indicating that all silicon–chloride bonds have been alkylated. Since polysilynes, like linear polysilanes, are degraded in both acidic and basic media, an equally important benefit of the capping titration is that it ensures the neutrality of the aqueous phase formed during workup.

This capping procedure would suggest the introduction of a substantial number of dialkylsilicon "edge groups" and trialkylsilicon end groups, but NMR and analytical data on the purified high molecular weight polymers (vide infra) suggest that these represent <2% the total (SiR_x) units. A volatile low molecular weight component recovered from crude poly(*n*-butylsilyne) exhibited methyl to butyl ratios of up to 2. It appears that under the conditions employed the monomer units are added to the growing polymer with complete reduction, rather than assembling into partially chlorinated intermediates.

Polysilyne purification is accomplished by dissolution of the polymers in THF and sequential precipitation with water, methanol, and ethanol. Although this procedure does decrease polydispersity by removing some lower molecular weight fractions, GPC analyses of the crude reaction mixtures reveal surprisingly few oligomers. A more important effect of this purification procedure is the removal of occluded alkali metal and magnesium salts, since simple washing of the hydrophobic polymers with water is ineffective. X-ray fluorescence analysis of crude polymers typically indicates approximately 1% chloride (by weight), which is reduced after two precipitations to approximately 0.1%.

Good solvation of the reaction intermediates was found to be necessary to ensure their complete reduction. Because the alkyltrichlorosilane monomers are stable only in hydrocarbons, a longer chain alkyl substituent is required to keep the reaction intermediates soluble. However, it was found that subsequent addition of a more polar solvent was necessary to effect complete reduction of chlorinated polymeric intermediates. When *n*-butyltrichlorosilane was sonochemically reduced in pentane without the subsequent addition of THF, the resulting polymer contained about 2% residual chloride, as opposed to less than about 0.1% usually found in poly(*n*-butylsilyne) prepared by using the pentane/THF procedure. Similarly, a preparation of poly(*n*-hexylsilyne) in pentane alone gave only oily, oligomeric product which slowly evolved HCl on hydrolysis, indicating the presence of unreacted silicon–chloride bonds. Good solvation of the reaction intermediates is perhaps the most important factor in the successful synthesis of polysilynes.

High-intensity ultrasonic irradiation facilitates the formation of poly(alkylsilynes) in a number of ways. Emulsification of the reductant prevents surface passivation and ensures its quantitative reaction, thereby providing exact control of the reducing agent/monomer stoichiometry. Another effect of homogenizing the reaction mixture may be to promote more uniform reduction and assembly

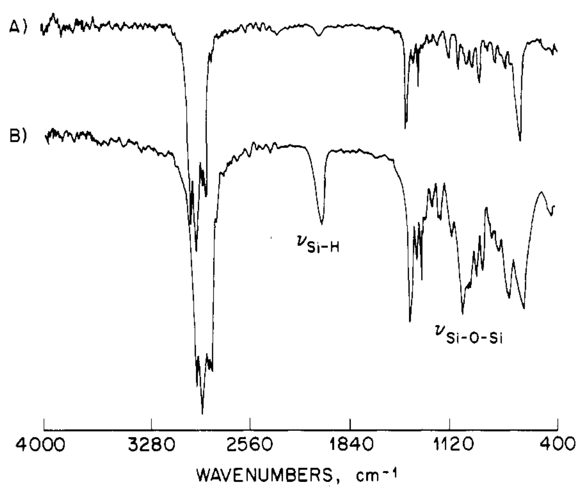

Figure 1. Comparison of IR spectra of poly(n-hexylsilyne) prepared with (A) an ultrasonically generated NaK emulsion and (B) unemulsified NaK.

of the monomers into soluble networks without occlusion of unreacted Si–Cl sites. The reaction of the NaK emulsion appears instantaneous but is more readily controlled, avoiding local overreduction and depolymerization. These effects are illustrated in Figure 1, which compares the IR spectrum of poly(n-hexylsilyne) made by ultrasonically irradiating the NaK/monomer reaction mixture with the spectrum of poly(n-hexylsilyne) synthesized by simple stirring of the reaction mixture for the same time period. After similar workup, the unsonicated polymer shows both a strong siloxane band, arising from hydrolysis of unreduced silicon–chlorine bonds, and a large silicon–hydride band, attributable to protonation of silyl anions arising from overreduction. While this material is initially tractable, it rapidly becomes insoluble upon storage.

Physical and Spectral Properties of Polysilynes. The poly(alkylsilynes) are all isolated as yellow, moderately air- and light-sensitive powders that remain freely soluble in nonpolar organic solvents, from which they can be cast or spun into transparent films. IR spectra of the polymers prepared by using the optimized pentane–95% NaK–THF–RMgCl procedure show no significant Si–H and Si–O–Si bands, and, with the exception of the less soluble poly(n-propylsilyne), chemical analyses correct for the empirical formula $(SiR)_n$ were obtained. The yields of purified poly(n-butylsilyne) and poly(n-hexylsilyne) ranged from 11% to 35%. Molecular weights versus polystyrene, as determined by gel permeation chromatography, are between 17 000 and 24 000 for poly(n-butylsilyne) and poly(n-hexylsilyne); the hexane-soluble fraction of poly(n-propylsilyne) (vide infra) had mean GPC molecular weights between 3000 and 8000. Actual molecular weights, as determined by light scattering, appear to be approximately 4 times greater than those determined by GPC.[16] In contrast to the linear polysilanes, isolated poly(n-butylsilyne) with a GPC $\bar{M}_w = 17\,000$ did not significantly degrade under full power sonication for 15 min.[17]

The choice of alkyl substituent has a major effect on the properties of the poly(alkylsilynes). As was the case with linear polysilanes,[1] the solubility of the polymers decreases with decreasing chain length of the n-alkyl substituents. While poly(n-hexylsilyne) is extremely soluble in organic solvents, only the low molecular weight ($\bar{M}_w \leq 8000$) fraction of poly(n-propylsilyne) is readily soluble, and material obtained from the reduction of methyltrichlorosilane is completely intractable. Changing the steric requirements of the alkyl substituent also appears to affect the degree of polymerization attainable. For example, the reductive condensation of t-butyltrichlorosilane gave only oligomeric material ($\bar{M}_w = 350$),[18] suggesting that bulkier groups may inhibit formation of an extensive polysilyne network. Conversely, the hydrocarbon-insoluble fraction of poly(n-propylsilyne) (**4a**) had $\bar{M}_w = 1.5 \times 10^5$ and a high polydispersity. Such high molecular weight fractions are not observed in the polysilynes with larger alkyl substituents; possibly the smaller n-propyl substituent allows more extensive formation of a cagelike network while longer n-alkyl groups favor sheetlike structures.

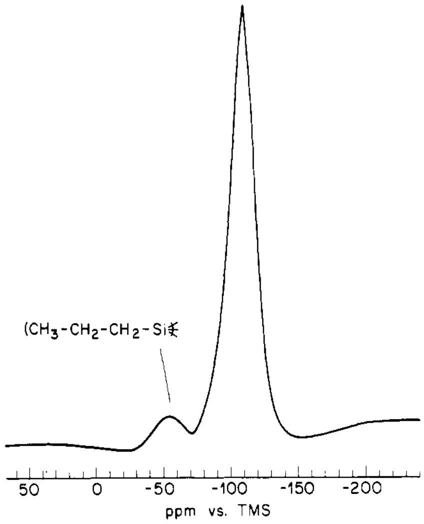

Figure 2. ^{29}Si NMR spectrum of poly(n-propylsilyne) **4b** in C_6D_6 solution. Number of transients = 15 240. The large peak at $\delta = -110$ ppm is the glass resonance of the sample tube and probe insert.

X-ray fluorescence analyses on the insoluble "poly(methylsilyne)" and the hydrocarbon-insoluble fraction of poly(n-propylsilyne) (**4a**) indicated about 3–4% chloride by weight, while the hydrocarbon-soluble propyl polymer **4b** contained less than 0.1% chloride. Some residual chloride may be present as occluded alkali metal and magnesium salts that cannot be efficiently removed unless the polymer can be dissolved and precipitated. Incomplete reduction of silicon–chloride bonds may also be a cause of the high chloride content.

X-ray powder pattern analyses of the poly(alkylsilynes) were featureless, which suggests that the polymers adopt amorphous, glasslike structures. The poly(alkylsilynes) are moderately sensitive to oxygen in the presence of light but are thermally stable to 300 °C. Pyrolysis mass spectra at this temperature show only the respective 1-alkene and smaller alkyl fragments, and no major silicon-containing fragments are volatilized. In contrast, mass spectra of poly(n-hexylmethylsilane)[19] and poly(dimethylsilane)–poly(phenylmethylsilane) 1:1 copolymer[5] showed fragmentation into a variety of silylene and higher oligomeric components. This difference in pyrolysis behavior can be directly related to the difference in structure of the two classes of polymers. Poly(alkylsilynes), due to their 1:1 silicon/alkyl stoichiometry, cannot extrude stable dialkylsilylene fragments, and their network structure appears to enforce the retention of silicon atoms.

NMR Studies of Poly(alkylsilynes). NMR provides the most direct information about the microstructure of the poly(alkylsilynes). The ^{29}Si solution NMR spectra of all three polymers exhibit one very broad, weak resonance at approximately −55 to −58 ppm (Figure 2). The solid-state ^{29}Si NMR spectra show similar large, broad resonances between −55 and −65 ppm and minor peaks between +30 and −30 ppm (Figure 3). The minor peaks are of much greater relative intensity in the spectrum of

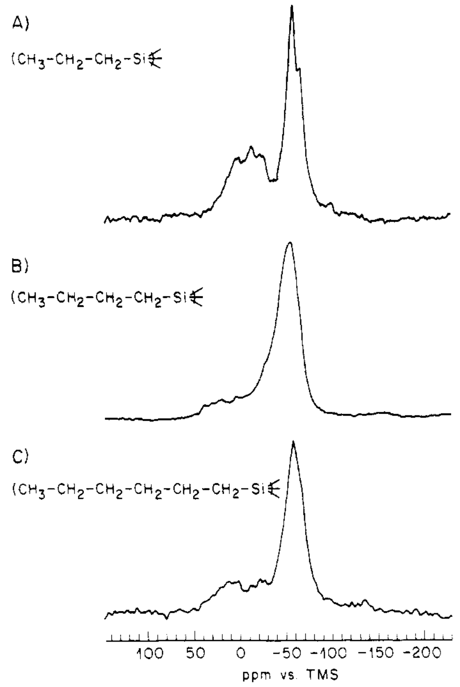

Figure 3. CPMAS ^{29}Si NMR spectra of poly(alkylsilynes): (A) poly(*n*-propylsilyne) **4a**; (B) poly(*n*-butylsilyne); (C) poly(*n*-hexylsilyne).

Table II
^{29}Si Chemical Shifts for Silanes of Varying Degrees of Silyl Substitution

no. of silyl substituents	compd	δ(^{29}Si)[a]	ref
2	poly(di-*n*-hexylsilane)	−24.8	2a
	poly(methylphenylsilane)	−39	19
	poly(methylhexylsilane)	−32.0	2a
3	polyhexylsilyne (1)	−57 (solution)	this work
		−60 (solid)	this work
	(hexyl)Si(SiMe$_3$)$_3$	−74.8	19
	(phenyl)Si(SiMe$_3$)$_3$	−74.2	19
4	Si(SiMe$_3$)$_4$	−135.5	21
sp^2	(Mes)$_2$Si=Si(Mes)$_2$[b]	+63.6	23a,b
	(Mes)(*t*-Bu)Si=Si(*t*-*bu*)(Mes)	+90.3 (trans) +94.7 (cis)	23a 23a
	(*t*-Bu)$_2$Si=Si(*t*-Bu)$_2$	+64.06	23c

[a] In ppm versus tetramethylsilane. [b] Mes = mesityl.

poly(*n*-propylsilyne). The chemical shifts of the major resonances are most characteristic of tetrahedral silicons, which have three silyl substituents (Table II). Disilyl-substituted silicons fall in the chemical shift range −20 to −40 ppm;[2a,18] trisilyl-substituted silicons are reported from −70 to −90 ppm[18,20] and tetrasilyl-substituted silicons from −80 to −130 ppm.[20,21] The downfield shift of the ^{29}Si resonance of the poly(alkylsilynes) compared to that of trisubstituted model compounds may be attributed to electronic long-range effects of the alkyl groups, a structure with a high degree of cyclic character,[22] and extensive σ-conjugation.

The major component of the polysilyne backbone is therefore indicated to consist of alkylsilicon units in which each silicon atom is σ-bonded to three other silicons. The minor resonances seen at −10 to −30 ppm in the solid-state ^{29}Si NMR are attributed to silicon–dialkyl "edge groups", which as disilyl-substituted silicons should fall into this chemical shift range. Further downfield resonances are evident in the ^{29}Si NMR of the insoluble fraction of the poly(*n*-propylsilyne) product, which may result from unreduced silicon–chloride sites.

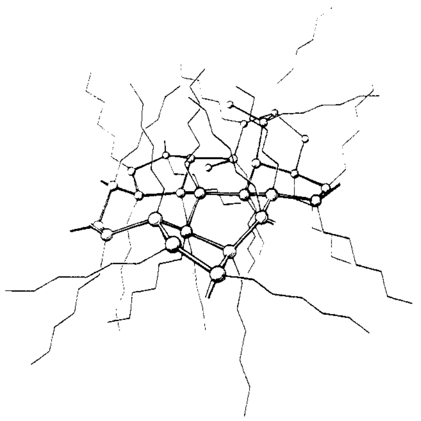

Figure 4. Schematic representation of a probable structural description for poly(*n*-hexylsilyne).

No ^{29}Si signal is observed in either the solution or solid-state NMR spectra of the poly(alkylsilynes) at +60 to +90 ppm, the region where resonances of silicon–silicon double bonds occur[23] (Table II). Although ^{29}Si chemicalshifts have been determined only for isolated silicon–silicon double bonds, both the lack of any signal in this region and electronic spectral data (vide infra) eliminate Si=Si bonds and thus a linear polyacetylene-like configuration as primary structural features of polysilynes. This is consistent with the decreased tendency of silicon, as opposed to carbon, to form π-bonds.

The broadness of the CPMAS ^{29}Si NMR resonances of the poly(alkylsilynes) is consistent with a wide variety of chemical environments, such as is seen in the ^{29}Si MAS NMR spectra of amorphous silicon carbide[24] and silicate glasses. The low intensity and broadness of the solution silicon NMR resonance indicate a very rigid backbone. This is consistent with a randomly constructed network structure of sheets or cages of fused rings (Figure 4), a structural intermediate between that of linear polysilanes and elemental silicon.

The ^{1}H and ^{13}C NMR spectra of poly(alkylsilynes) also indicate rigid polymer networks and suggest wide varieties of chemical environments. Their solution ^{1}H NMR spectra consist of broad signals in the expected alkyl region, while the resonances for protons on each carbon are clearly resolved in the ^{1}H spectra of linear polysilanes.[2a] In solution, the line widths of the ^{13}C NMR resonances of the poly(alkylsilynes) increase progressing inward along the alkyl chains to a far greater extent than is seen in linear polysilanes.[2a] In the solution spectra of all three polysilynes, the C$_1$ carbon resonance is broad and unresolved (Figure 5C).

Figure 5 shows a comparison of the solution ^{13}C NMR spectra of poly(hexylmethylsilane), poly(*n*-hexylsilyne), and poly(hexylsilsesquioxane), (C$_6$H$_{13}$SiO$_{1.5}$)$_n$, a randomly branched network siloxane ("T-resin").[18] The hexyl group of the polysilane displays sharp, unperturbed resonances (Figure 5A). The disordered network structure of the siloxane T-resin is reflected in the polymer's ^{13}C NMR spectrum, in which the resonances of the hexyl group begin to show broadening and chemical shift differences at the C$_2$ and C$_1$ carbons as compared to the linear polysilane (Figure 5B). However, the Si–O–Si linkages of the T-resin impart both more flexibility to the polymer backbone and, due to the insulating oxygen atoms, more uniform electronic environments to the alkyl chain compared to the poly(alkylsilynes). The greater rigidity and variety of chemical environments (particularly for C$_1$ to C$_3$) found in poly(alkylsilynes) are seen in the ^{13}C NMR spectra of

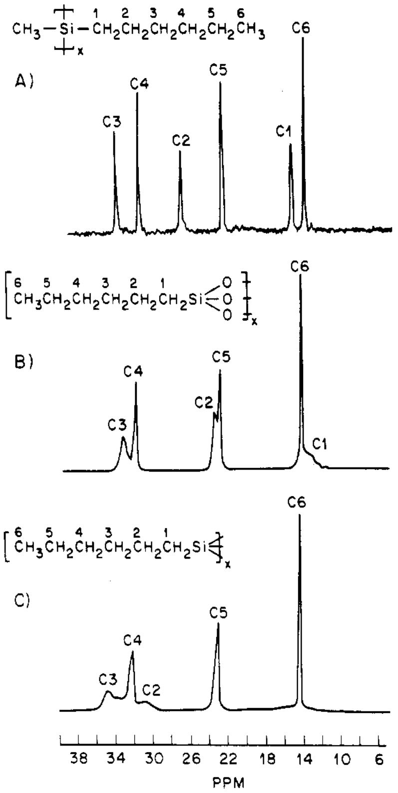

Figure 5. ^{13}C NMR spectra of linear and network silicon polymers in C_6D_6 solution: (A) poly(hexylmethylsilane); (B) poly(hexylsilsesquioxane) (T-resin); (C) poly(*n*-hexylsilyne).

poly(*n*-hexylsilyne) (Figure 5C), where the C_3 and C_2 resonances are greatly broadened and the C_1 resonance has become unresolvable from the baseline. The ^{13}C NMR spectra of poly(*n*-butylsilyne) and the hexane-soluble poly(*n*-propylsilyne) show similar effects.

The solid-state ^{13}C NMR spectra of the polysilynes are similar in appearance to the solution spectra (Figure 6), showing no resolvable C_1 carbon resonance but only a broad baseline feature. The C_2 carbon resonance is more difficult to resolve compared to the solution spectra. The same line-width behavior observed in solution (i.e., progressive broadening of the lines) is also seen in the solid state. The degree of broadening is similar to that observed for the conformationally disordered phase of poly(di-*n*-hexylsilane),[2b] indicating that conformational averaging is occurring in the polysilynes as well. Without cross-polarization, the MAS ^{13}C resonances of the polysilynes are weaker in intensity, but the same chemical shifts are observed. The solid-state NMR data therefore provide no evidence for the presence of distinct phases in these samples.

ESR Studies. While the solution ESR signal of poly(*n*-hexylsilyne) at room temperature is barely detectable, when NaK alloy is added the solution becomes deep red and a strong ESR signal appears. The *g* value is 2.0037, consistent with those observed for cyclic silicon-centered radical anions.[9a,9b,22b] A line-shape analysis did not suggest complete electron delocalization, but the lack of fine structure suggested electron mobility among a multiplicity of environments. Similar silicon-centered radical anions were formed upon chemical or electrochemical reduction of many cyclic oligomeric diorganosilanes.[9a,9b,22b]

Electronic Spectra and Photochemistry of Poly(alkylsilynes). While the linear diorganopolysilanes exhibit strong σ–σ^* transitions (λ_{max} = 300–350 nm, ϵ = 2800–12000 per Si) in the near UV,[1] solutions of poly(alkylsilynes) exhibit an even more intense broad absorption from $\lambda \le 200$ nm tailing down into the visible (Figure 7). The very high extinction coefficient per silicon fragment (ϵ = 28000–35000 at 200 nm) of poly(alkylsilynes) may be attributed to an extension of Si–Si σ-"conjugation" effects observed in polysilanes into three dimensions across the polysilyne networks.

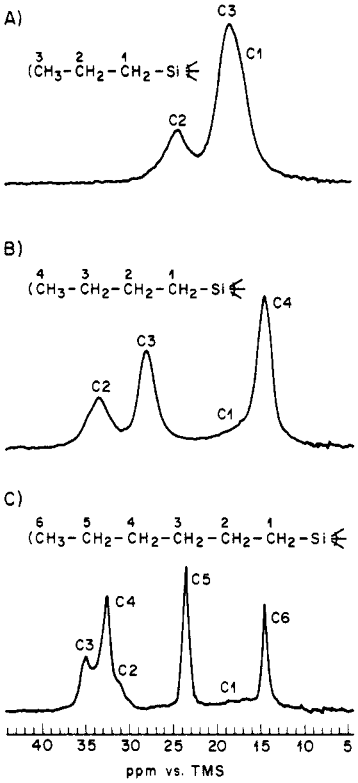

Figure 6. CPMAS ^{13}C NMR spectra of poly(alkylsilynes): (A) poly(*n*-propylsilyne) **4a**; (B) poly(*n*-butylsilyne); (C) poly(*n*-hexylsilyne).

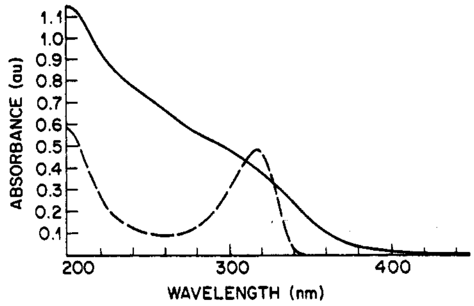

Figure 7. Comparison of the electronic spectra of poly(*n*-hexylsilyne) (solid line) and poly(di-*n*-hexylsilane) (dashed line) as 4×10^{-5} M solutions in cyclohexane.

Since silicon–silicon double-bonded compounds exhibit intense absorptions between 400 and 440 nm,[23,25] the absence of a resolvable absorption in this region provides additional evidence that silicon–silicon double bonds are not a primary structural component of poly(alkylsilynes).

Conclusions

The synthesis of the first $(RSi)_n$ network polymers, or poly(alkylsilynes), was achieved by careful selection of monomer, reductant, and solvents in a sonochemically mediated reductive condensation procedure. The new polymers (with R = *n*-propyl, *n*-butyl, and *n*-hexyl) remain soluble in nonpolar organic solvents and are readily cast into amorphous, transparent yellow films. All chemical and spectroscopic data indicate that the polysilynes are constructed primarily of sp^3-hybridized alkylsilicon units assembled via Si–Si bonds into irregular networks. Thus the polysilynes provide the first examples of soluble σ-delocalized materials with a composition intermediate between that of linear polysilanes and elemental silicon. Investigations into the properties and potential applications of these and related new materials are in progress.

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Registry No. 1 (SRU), 94904-85-5; 1 (homopolymer), 97036-67-4; 2 (homopolymer), 118018-35-2; 3 (homopolymer), 118018-36-3; 4 (homopolymer), 118018-37-4; NaK, 11135-81-2; poly(phenylmethylsilane) (SRU), 76188-55-1; poly(phenylmethylsilane) (homopolymer), 31324-77-3.

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(11) Heat Systems-Ultrasonics Inc. Model 375 W generator with high-intensity convertor with standard $^1/_2$-in. D titanium immersion horn. The generator was connected via a high-voltage electrical feedthrough to the convertor located inside the glovebox.

(12) If the pH of the hydrolyzed reaction mixture was not exactly neutral, a buffer solution such as 1.0 M $NaHCO_3$ was used instead of water.

(13) If the polymer remained in solution in the organic phase, the layers were quickly separated and methanol was added to the organic layer. The precipitated polymer was collected by filtration and purified as stated.

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Hydrogen–Deuterium Exchange for Labeling Polyethylene

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ABSTRACT: Hydrogen–deuterium exchange on linear polyethylene is achieved with a heterogeneous rhodium catalyst. Results are presented for nearly monodisperse and whole polymers with fractional deuteration $y \approx 0.2$–0.3, although $y = 0.6$ can be obtained. The exchange reaction appears statistically uniform and causes little or no change in the degree of polymerization. Small-angle neutron-scattering intensities indicate ideal mixtures of exchanged and unexchanged molecules, with some excess concentration fluctuations being seen in the semicrystalline whole polymer. The isotopic interaction parameter, χ_{hd}, is evaluated as a function of average deuterium fraction, y.

Introduction

Small-angle neutron scattering (SANS) has evolved as a powerful method for studying such features as chain dimensions and thermodynamic interactions of polymers, particularly in condensed or highly concentrated systems. Virtually all experiments employ deuteration of one component to achieve contrast for sufficient scattered intensity. Preparation of "labeled" chains can be accomplished by

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