Synthesis of an Ordered Structurally Periodic Polysilane, $(Me_2Si\text{-}n\text{-}Hex_2SiMe_2Si)_n$

Polysilanes[1] have been extensively studied in the past few years because of their potential applications in areas such as microlithography,[2] ceramics,[3] photoconductivity,[4] photoinitiation,[5] and nonlinear optics.[6] These polymers exhibit delocalization of σ electrons along the polymer backbone as shown by their strong absorption bands in the ultraviolet region. We report here the first synthesis of a polysilane with an ordered periodic backbone structure, **3a**.

The usual synthesis of polysilane copolymers by cocondensation of different dichlorosilanes with sodium in refluxing toluene leads to random or blocklike arrangements. Previous polysilane syntheses from dihalodisilanes[7] (e.g., 1,2-dichlorophenyltrimethyldisilane) or dihalotrisilanes[8] (e.g., 1,3-dichloro-2,2-di-*n*-butyltetramethyltrisilane) containing different substituent groups have also produced random polymers due to lack of regioselectivity and/or randomization by cleavage of the original Si–Si bonds in the precursor. Randomization is not surprising since silicon anions, postulated intermediates in the process of polymerization, are known to cleave Si–Si bonds in small molecules.[9]

We have synthesized the precursor **2** in two steps according to eq 1. (Dimethylphenylsilyl)lithium in THF was added dropwise to a solution of di-*n*-hexyldichlorosilane in THF cooled to 0 °C giving 2,2-di-*n*-hexyl-1,3-diphenyltetramethyltrisilane (**1**) in 55% yield. Bromodephenylation of **1** in benzene with HBr and $AlBr_3$ gave 1,3-dibromo-2,2-di-*n*-hexyltetramethyltrisilane (**2**) in 88% yield. Both **1** and **2** were characterized by ^{29}Si, ^{13}C, and ^1H NMR, mass spectroscopy, and elemental analysis. The polymerization was done by dropwise addition of a Na/K alloy into a stirred toluene solution of **2** in 25% excess at 90 °C; the solvent refluxed as the reaction proceeded.

A bimodal molecular weight distribution of polymer **3** was obtained in 6% yield.[10] The high and low molecular weight portions were fractionated from toluene by addition of 2-propanol. The high molecular weight fraction **3b** (M_w = 830 000, PD = 1.7, 3% yield)[11] is partially randomized as shown by its ^{29}Si NMR spectrum in Figure 1b. The multiple peaks near −36 ppm for Me_2Si and −26 ppm for $n\text{-}Hex_2Si$ demonstrate that the original Si–Si bonds of **2** have been broken and reformed in a different sequence. The low molecular weight fraction **3a** (M_w = 8500, PD = 1.4, 3% yield) represents an ordered polysilane, the first of its type, with an AABAABAAB arrangement. The ^{29}Si NMR in Figure 1a shows two single peaks corresponding to the Me_2Si (−36 ppm) and $n\text{-}Hex_2Si$ (−26 ppm) units as expected from a periodic polymer of this type. For comparison a random copolymer was synthesized by cocondensation of dichlorodimethylsilane and dichlorodi-*n*-hexylsilane; it shows two broad peaks in the ^{29}Si NMR (Figure 1c).[12]

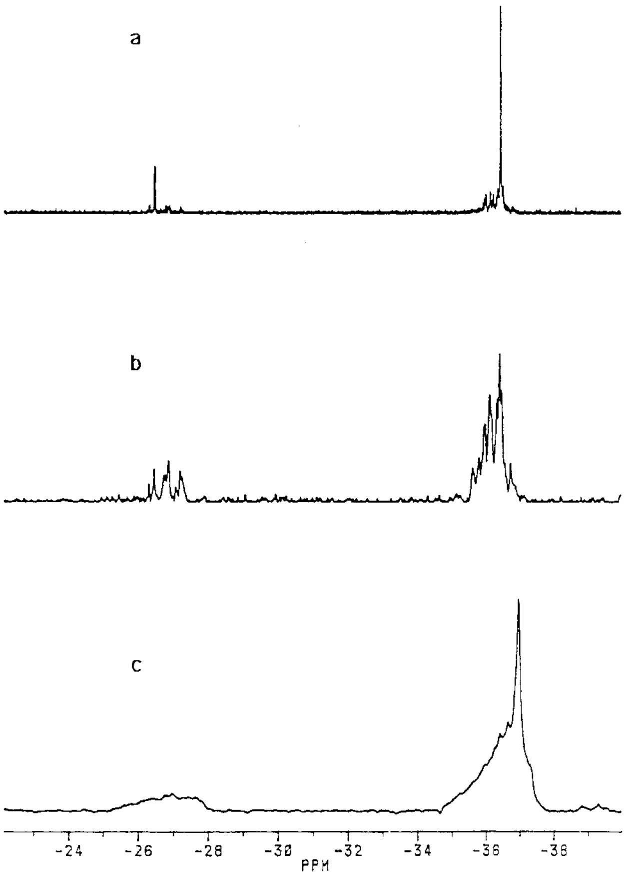
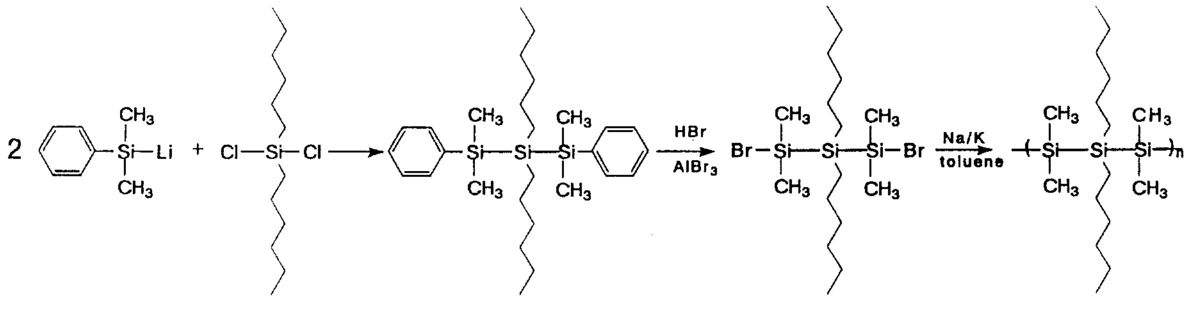


Figure 1. ^{29}Si INEPT NMR spectra in benzene-d_6 of (a) ordered periodic LMW polysilane **3a**, $(Me_2Si(n\text{-}Hex)_2SiMe_2Si)_n$; (b) partially randomized HMW polysilane **3b**, $(Me_2Si(n\text{-}Hex)_2SiMe_2Si)_n$; and (c) random silane copolymer, $(Me_2Si)_m\text{-}((n\text{-}Hex_2)Si)_n$.

The difference in order between the two fractions suggests that they are formed either by a different mechanism or in different environments, possibly at the sodium surface and in solution. We suggest that the low molecular weight ordered fraction results from diffusion of the chains away from the metal surface into solution and ceasing of growth before any significant randomization takes place. The high molecular weight fraction may result from growth at the sodium surface; it is common that above a certain molecular weight the rates of diffusion of macromolecules decrease sharply as a result of chain entanglement. The surface of the sodium is where the concentration of silicon anions is greatest and therefore where cleavage is more likely to occur. The idea of diffusion of low molecular weight chains into solution and entanglement as the chains grow at the metal surface is strongly supported by recent experiments that correlate the molecular weight distribution with the size of the sub-



(1)

1 2 3a + 3b

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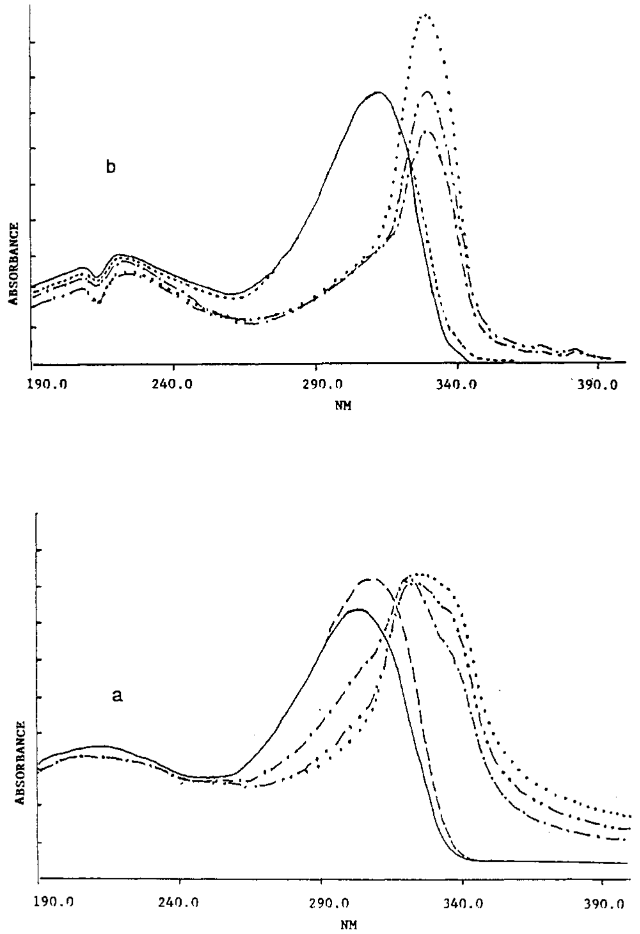

Figure 2. UV spectra in THF. (a) Periodic LMW polysilane **3a**: (—) 25 °C; (- - -) -40 °C; (- · -) -70 °C; (- · · · -) -80 °C; (· · ·) -90 °C. (b) Partially randomized HMW polysilane **3b**: (—) 25 °C; (- - -) -40 °C; (- · -) -60 °C; (- · · · -) -80 °C; (· · ·) -100 °C.

stituent on silicon.[13]

It is interesting to note the difference in the first-order transition temperatures obtained by differential scanning calorimetry (DSC), where the microcrystals of **3a** melt at 90 °C and those of **3b** at 53 °C. This correlates well with data from cross-polarized microscopy, which showed for **3a** very well-defined crystals with maltese cross patterns below 90 °C and an isotropic melt above that temperature. Polymer **3b** is very birefringent below 53 °C, but the crystallites are small and no defined crystal patterns could be observed under the cross-polarized microscope. Birefringence disappears above 53 °C at the isotropic melt.

A striking difference was observed in the thermochromic behavior of the two fractions in THF solution. Like many other polysilanes,[14,15] both **3a** and **3b** show an abrupt bathochromic shift, over a small temperature range, in the UV absorption spectra upon cooling. This has been explained by an increase in the population of trans segments in a coil to rod type transition.[1] In THF, the random fraction **3b** absorbs at 307 nm at 25 °C and 326 nm at -100 °C with an abrupt shift around -50 °C (Figure 2b). For the ordered fraction **3a**, λ_{max} changed from 306 nm at 25 °C to 321 nm at -100 °C with an abrupt shift between -50 and -60 °C. At -70 °C, however, another absorption band appears at 331 nm and grows in intensity as the temperature is lowered to -100 °C (Figure 2a). The origin of this new absorption band is still uncertain but probably reflects the ordered periodic nature of the polymer.[16]

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(11) Molecular weights were measured by GPC by using polystyrene standards.
(12) Polymerization of 2 was also carried out under standard conditions (addition of the 1,3-dibromotrisilane to a Na dispersion in boiling toluene). The polymeric product had a bimodal molecular weight distribution where the low molecular weight fraction was randomized, although to a lesser extent than the high molecular weight portion. In order to minimize randomization and obtain **3a**, it was necessary to use an excess of monomer and inverse addition (dropwise addition of Na/K into the monomer solution).
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