# Synthesis of Polysilanes in High Yields and in Optically Active Solvents

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## 1. Introduction

Polysilanes (Figure 1) are linear chain polymers whose backbones are made entirely from silicon atoms. The $R_1$ and $R_2$ groups attached to the silicon are usually aryl or alkyl. The unusual feature that the polysilane structure has is that the uninterrupted run of silicon atoms can facilitate significant delocalisation along the silicon framework (σ-conjugation). As a result, these materials have several potential applications such as preceramic precursors, photoconductors, photoinitiators in vinyl polymerisations, photoresists and more recently as non linear optical materials [1].

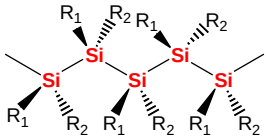



Figure 1: Structure of polysilanes

## 2. Experimental Section

**Materials**: THF was dried over $MgSO_4$ for at least 24 hours and then dried over sodium wire for at least 24 hours before distillation over sodium wire and benzophenone under nitrogen immediately prior to use. Dichloromethyl-*n*-hexylsilane (Gelest) dichlorodi-*n*-hexylsilane (Fluorochem) and dichloromethylpropylsilane (Fluorochem) were distilled under reduced pressure and stored at 4ºC under nitrogen. Methanol (99.99% Fisher) was used as received. Sodium (Lancaster, 99%) was stored under paraffin oil and before use it was cut and washed under freshly distilled toluene. Sodium dispersions were prepared immediately prior to use by heating the freshly cut metal in distilled toluene under reflux before dispersing it into fine sand through the use of homogeniser (Ultra Turax T8, homogeniser, IKA Labortechnik). The toluene was removed under vacuum. All glassware was flamed dried under vacuum prior to use.

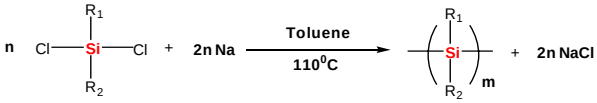
**Synthesis of Poly(methyl-n-hexylsilane):**A typical PHMS synthesis is as follows. To a two-necked round bottom flask (250 ml) equipped with an egg-shaped PTFE stirring bar and a condenser, freshly cut sodium metal (2.4 g, 0.1 mol) was added under a nitrogen atmosphere using Schlenk-line techniques. The sodium was transformed to a fine dispersion as outlined above. To the sodium dispersion, THF (60 ml) followed dichloro-*n*-hexylmethylsilane (9.93 g, 0.05 mol) were added via a syringe. The reaction was then stirred rapidly at room temperature for 22 hours. Termination was achieved by the slow addition of methanol followed by the addition of excess methanol (>100 ml). After quenching the reaction, methanol was removed and water (100 ml) was added to dissolve NaCl . The polymer was then dissolved in either toluene (dichloromethane for experiment 1) (excess) and after rapid stirring the mixture was placed in a separating funnel. After rapid shaking, the two layers were separated. The solvent layer was kept and water was washed 3-4 times with the organic solvent, to remove any polymer traces left in the water. The solution was dried for 2 hours under magnesium sulphate, filtered and the solvent removed under vacuum. Further purification (to remove Fraction I and isolate the pure linear product) was achieved by repeated precipitations by slowly adding a THF solution of the crude polymer dropwise to rapidly stirred isopropanol( 40 ml) two times.

**Synthesis of Poly(di-n-hexylsilane):** Same method was used as above.

**Analyses.** NMR spectra were recorded in $CDCl_3$ at 30ºC with a JEOL GX-270 spectrometer.UV-vis spectra were recorded in THF (1.2 x $10^{-4}$mol Si-unit $dm^{-3}$ for PHMS, 9.5 x $10^{-5}$ mol Si- unit $dm^{-3}$ for PDHS) solutions on a Heλios β Unicam UV Spectrometer. IR spectra were recorded in solid as a thin film with a Avatar 360 FT- IR. The molecular weights and polydispersity values were measured using equipment supplied by Polymer Laboratories Ltd. All measurements were carried out at 400C using two 300 x 7.5 mm Plgel μm Mixed-C columns equipped with a LC 1120 HPLC pump and a Shodex RI-101 refractive index detector. The instrumentation was calibrated using polystyrene standards supplied from Polymer laboratories Ltd.

## 3. High Yield Synthesis of Polydialkylsilanes

Under standard Wurtz reductive coupling conditions (Na in refluxing toluene) (Scheme 1) the maximum crude yield reported of poly(n-hexylmethylsilane) obtained to date has been 15% and the maximum crude yield of poly(di-n-hexylsilane) was 37% by Miller et al [2]. In 1998 Jones and co-workers demonstrated that polymethylphenylsilane can be synthesised in high crude yields of 80% using the Wurtz reductive polymerisation in THF at room temperature. In this presentation we will demonstrate the generality of the room temperature polymerisation of these two representative polymers that gave crude yields > 60% and isolated yields > 50% [3,4].




Scheme 1

The table below show the crude and isolated yield of these two polymers and polypropylmethylsilane (PMPrS) as well as the molecular weights and polydispersities.

Table 1: Yields and molecular weight characteristics of polysilanes

| Polymer | Crude polymer (%) | Isolated polymer (%) | Mw | Mn | PD |
|---|---|---|---|---|---|
| PHMS | 82 | 61 | 20000 | 31500 | 1.6 |
| PHMS | 67 | 52 | 8700 | 17700 | 2.0 |
| PDHS | 84 | 58 | 48900 | 60500 | 1.4 |
| PDHS | 65 | 53 | 17200 | 42000 | 2.5 |

The effect of the monomer concentration was also investigated. Surprising a few studies have been reported in order to determine the role of monomer concentration on the Wurtz reductive polymerisation. We conducted experiments at three different monomer concentrations and we concluded that the monomer concentration does dramatically affect the molecular weights as well as the yields of the polymers and at higher concentration higher yields and molecular weights were achieved.

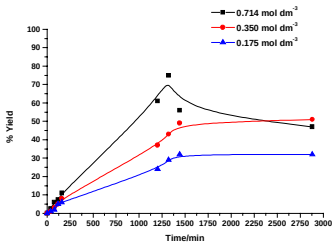



Figure 3: Crude yield (%) versus time on the synthesis of PHMS in THF at room temperature.

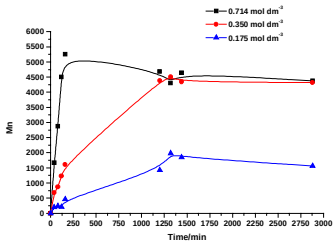



Figure 4: Mn versus time on the synthesis of PHMS in THF at room temperature.

## 4. Synthesis in Chiral Solvents

The main chain conformation of polysilanes is helical, but despite this, these polymers are not usually optically active. This is because both P- (plus) and M- (minus) screw helical turns are of equal energy and they both exist in equal proportions. But if the energies of P and M become unequal, the lowest energy screw sense will be preferentially populated and will be adopted by the main chain, therefore optical activity will be observed [5]. The same thing applies when the polymer is dissolved in a chiral solvent. The equilibrium is interrupted and one of the screw senses will predominate in solution. This phenomenon was firstly observed by Green et al when they dissolved poly(n-hexylisocyanate) in chlorinated chiral solvents [6]. The same phenomenon was also observed by Holder and co-workers when they dissolved polysilanes in chiral ethers [7].

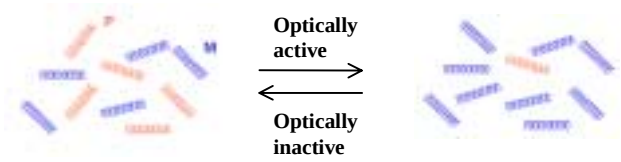



Figure 4: Peturbation of the balance of screw senses by chiral solvents

The molecular weight distribution of PMPS synthesised in refluxing toluene is usually trimodal (Figure 5). Fraction I is the low molecular weight material (thermodynamically stable) and it arises from the endbiting reaction at the beginning of the polymerisation or via backbiting reaction at any stage during the polymerisation. Fractions II (intermediate molecular weight) and III (high molecular weight) are the kinetic product (the linear polymer) and their origin is discussed below [8].

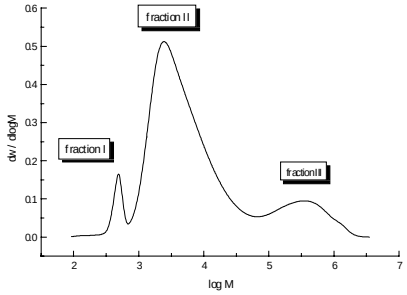
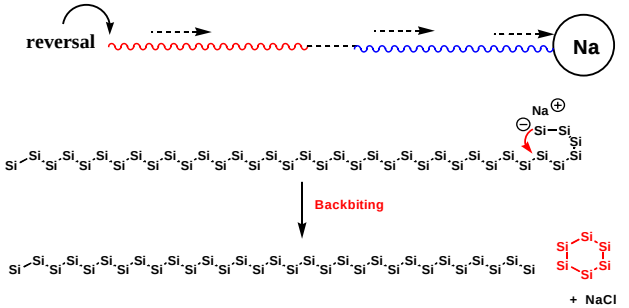


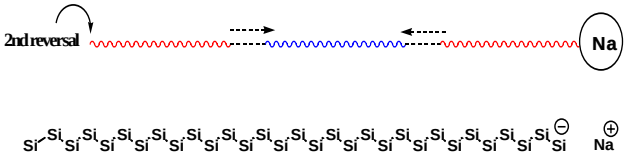

Figure 5: Molecular weight distribution of the synthesis of PMPS in refluxing toluene.

At the earliest stages of growth the polymer grows away from the metal's surface as a random coil consisting of a mixture of irregular P- and M- helical turns each separated from the next by a reversal ('defect') of the helix. The reversal diffuses rapidly in the chain sometime some reaching the surface of the metal. If this occur backbiting reaction will occur. The cyclic oligomer will be clipped off and the chain will be disengage from the chain (Scheme 2).
This is a termination step and the end product is Fraction II, the intermediate molecular weight. Maximum probability of this occurring is only when one reversal is present between the helical segments.




Scheme 2

When another reversal is added, two are present and there is a distinct probability of them 'cancelling' out. The chain growth continues and the end product is the high molecular weight material (Fraction III) (Scheme 3) [9].




Scheme 3

But what happens if the reaction is conducted in an optically active solvent? The polymer will grow away from the metal with one of the screw senses predominantly present. So the chance of a reversal being added between P- and M- screw senses is less, therefore the probability of the backbiting reaction to occur is minimised.
It can therefore be predicted that conducting the polymerisation in an optically active solvent will reduce chain termination and lead to increased yields of high molecular weight material.

We have synthesised polymethylphenylsilane in optically active and optically inactive limonene and we have investigated the effect that the optically active solvent has on the mechanism of Wurtz polymerisation and on the molecular weights of the polymers.
Firstly the experiments were conducted at room temperature. Little difference was observed in the molecular weights between the reaction products resulting from reactions conducted in the two solvents. But due to the fact that the backbiting reaction is thermally driven, experiments were conducted at $60^0$C. Preliminary results from the polymerisations conducted at this temperature show that backbiting reaction is affected by the chiral solvent, since higher molecular weight material is obtained in optically active solvent.

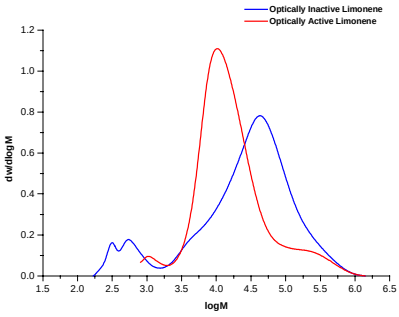



Figure 6: Molecular weight distribution of PMPS synthesised in (a): optically inactive limonene, (b): optically active limonene.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