1. Introduction

This chapter is primarily concerned with the synthesis and properties of functionalised polysilanes prepared by post-formation reactions of polysilanes. Modification of preformed polysilanes is of importance because of the limited number of substituent groups that can be used in the original polymer syntheses (see the earlier chapters in this section). In particular, the Wurtz reductive process, the most commonly used method of preparation, involves harsh reaction conditions. Not many substituents, other than alkyls or aryls, can survive exposure to molten sodium. The synthesis of polysilanes bearing a range of functional groups should facilitate their use in a number of the diverse applications described elsewhere in this book. The aims are the incorporation of electron-donating or electron-withdrawing substituents in order to modify the electronic properties of polysilanes and of hydrophilic or lipophobic groups to influence solubilities and surface properties [1]. For example, Yoshida et al. have prepared poly[1-(6-methoxyhexyl)-1,2,2-trimethyldisilylene], a polysilane with a functional side chain, (1), by the masked disilene method [2]. A monolayer of 1 displayed a unique chromism that reflects the hydrophilic/hydrophobic nature of the underlying substrate surface.

\[
\begin{align*}
&\text{Me}_3\text{Si}\left(\text{CH}_2\right)_{6}\text{OMe} \quad \text{Me}_3\text{Si}\left(\text{CH}_2\right)_{6}\text{OMe} \\
\text{Me}\quad \text{Si} &\quad \text{BuLi} \quad \text{EtOH} \\
\text{Ph} &\quad \text{Bu} \quad \left(\text{Me}\left(\text{CH}_2\right)_{6}\text{OMe}\right)_n \\
&m \quad \text{Si-Si} \quad \text{MeMe} \\
&n \quad \text{H}
\end{align*}
\]

Equation 1

A cast film of I showed an absorption maximum at 306 nm at 23°C but below 15°C a new band peaking at 328 nm started to grow. Langmuir-Blodgett (LB) films of I were prepared. The characteristic curve of the surface pressure-area isotherm per monomer unit of I on distilled water indicated the formation of a stable monolayer at the air/water interface. The monolayer could be transferred onto both a clean hydrophilic quartz plate and a hydrophobic one treated with hexamethyldisilazane by the conventional vertical dipping method. Interestingly, the monolayer of I deposited on a hydrophobic quartz plate showed a broad UV absorption at 306 nm, which was in agreement with the value obtained for the cast film at room temperature. In contrast, the absorption maximum on a hydrophilic quartz plate shifted to 322 nm and the width of absorption became substantially narrower. The shape of the UV absorption spectrum obtained on the water surface resembled that observed for the hydrophilic surface at 334 nm.

These results indicate that the conformations of the transferred monolayer of I on the hydrophobic and hydrophilic surfaces correspond to those in the cast film and on the water surface, respectively. This is a new type of chromism induced by hydrophilic surface properties. The anionic polymerisation of masked disilenes is a powerful method for preparing such polymers.

Yoshida et al. [3] have further demonstrated a novel piezo-chromism and a switching behaviour of in-plane surface orientation of functional polysilane I at the air/water interface. These investigations demonstrated that the combination of a hydrogen bond interaction and a surface pressure will considerably affect not only the conformation of the individual polysilane chain but also the two-dimensional structure of aggregates at the air/water interface.

2. Incorporation of Organic Substituents

In the following sub-sections the preparation of polysilanes which have been functionalised post-synthesis with organic substituents is discussed. The synthetic methods can be divided into those involving substitution/addition directly on the silicon backbone (Sections 2.1 - 2.3) and those in which the modification is performed at some more remote part of the polymer (Sections 2.4 - 2.6). It is important to bear in mind that the methods of functionalisation are limited by the somewhat fragile nature of the silicon-silicon bond. For example, even a catalytic amount of a sufficiently strong nucleophile may lead to complete degradation of a high polymer to low molecular weight cyclics [4].

2.1. HYDROSILYLATION REACTIONS

Functional groups [5] and crosslinking [6] can be introduced into polysilanes containing Si-H bonds by hydrosilylation reactions. For example, the following polymers can be prepared by the H2PtCl6 catalysed reaction of poly(methylsilane) with the appropriate unsaturated compounds [5].