

Polysilane Polymers — Chemistry and Spectroscopy

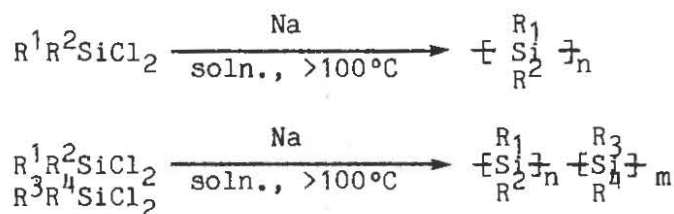
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Polysilanes are a class of inorganic polymers with a Si-Si backbone first reported by Kipping [1]. However, the first polysilanes synthesized by Kipping and later by Burkhard [2] were intractable and therefore little is known about their chemistry.

In 1975, Yajima and his coworkers discovered that the permethylpolysilane polymer was an excellent precursor for silicon carbide fibers [3] and this finding has led to a renewed interest in polysilane polymers. In 1980, soluble polysilane polymers were discovered independently by three different laboratories [4]. The silicon-silicon backbone of polysilanes is assembled by a Wurtz-type reductive condensation of the appropriate dichlorosilane monomer with highly dispersed sodium metal in a hydrocarbon diluent above 100°C [5]. Either homopolymer or copolymer can be made in this way:



The coupling reaction is strongly heterogeneous. The addition rate and the mode of reactant addition are crucial to the molecular weight and distribution of the polymer [6]. Other synthetic methods were also reported [7].

The uv spectra of polysilanes are characterized by a strong absorption in the 280-400 nm region [8] of the spectra.

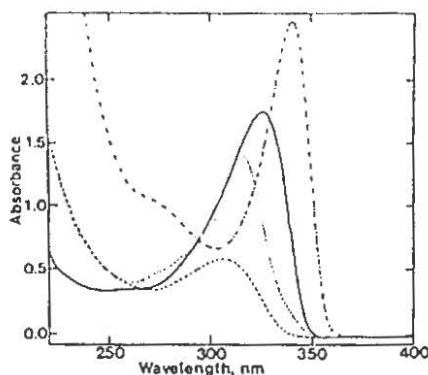


Fig. 1. uv spectra of representative polysilanes, 1 cm pathlength, concentration in mol-1 of Si-Si bonds in THF, —, (n-C12H25SiMe)_n, 1.1 × 10⁻⁴; ·····, (n-HexSiMe)_n, 1.3 × 10⁻⁴; —, (cyclo-HexSiMe)_n, 2.3 × 10⁻⁴ in cyclohexane; ·····, (PhSiMe)_n, 2.6 × 10⁻⁴.

Polymers $\text{[-R}^1\text{R}^2\text{Si-]}_n$ where $n > 20$ exhibit uv λ_{max} that are a function of the pendant organic groups. Polymers bearing aromatic substituents are red shifted from those with aliphatic substituents [9]. In addition, polymers $\text{[-R}^1\text{R}^2\text{Si-]}_n < 20$ exhibit a strong dependence of λ_{max} on the degree of polymerization [10]. This phenomenon was demonstrated by synthesizing polymers and oligomers of different chain lengths and is understood to result from increasing delocalization of electrons along the Si-Si backbone. Theoretical calculations based on Slater and Koster's LCAO show for polyalkylsilane polymers the transition is from σ of Si-3p_x (along the skeleton axis) AO's to the σ^* of Si-3s AO's, the band gap is around 4.5 eV compared to C-C single bond of about 8eV [11]. Polarized absorption spectra are consistent with this assignment [12]. Many polysilanes also show strong thermochromic behavior [13], which was explained as the side chain crystallization resulting in the conformational locking of the polymer backbone into a planar zig zag conformation. This conformational change was then responsible for the largest spectra red shift [14].

The high molecular weight polysilane derivatives are photochemically labile and the spectra bleaching is accompanied by a reduction in the polymer molecular weight [15]. In all cases Si-Si bond breaking is the photochemical predominant process, although concurrent crosslinking has been observed for derivatives with pendant unsaturation. The mechanism of this photodegradation involves silyl radicals and silylenes [16] as the primary reaction intermediates. The unique photochemistry with high quantum yields and nonlinear bleaching of polysilane polymers makes them usable as high resolution positive resists with excellent uv sensitivity [17].

Crosslinking of polysilane polymers is important for the use of these materials as precursors to ceramics. If the polymers are not crosslinked, most of the silicon is volatilized during thermolysis rather than remaining as silicon carbide. Generally, crosslinking can be induced by irradiation of a mixture of the polymer with a polyunsaturated crosslinking agent such as phenyltrivinylsilane. The free radicals generated upon photoscission add to the vinyl groups of the polyunsaturated compound to generate the crosslinking [6].

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