

Polysilanes: Their Synthesis, Properties and Application

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Although polydiphenylsilane [1] and polydimethylsilane [2] were synthesized earlier this century, there was little interest in these compounds because of their insolubility, intractability and highly crystalline nature. More recently, however, there has been a resurgence of interest in this area because of the discovery of soluble polysilane derivatives [3].

Linear homopolymers and copolymers are commonly synthesized according to a Wurtz-type coupling process,



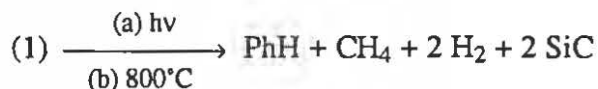
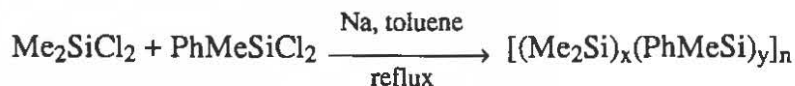
where R, R' = alkyl or aryl, but this method has several drawbacks including low yields of high molecular weight polymer, a bimodal molecular weight distribution and limited functional group tolerance [3,4,5,6]. It has been shown that sonochemical agitation of reaction mixtures results in a monomodal product distribution with a high yield of high molecular weight homopolymer, but this procedure seems to be valid only for aryl-substituted monomers [7]. Copolymers containing both alkyl and aryl substituents can also be synthesized using sonochemistry. Polysilanes, in general, are oxidatively and thermally stable to over 200°C, and many polysilanes can be melted and recast without decomposition [4].

The polysilanes exhibit a significant amount of electron delocalization and σ -conjugation along the silicon chains, and therefore, have some very interesting spectral properties [8,9,10]. All soluble, high-molecular weight polysilane derivatives absorb in the ultraviolet region, and the transition wavelength is highly dependent on the nature of the substituents [8]. The absorption is also dependent on the chain length, or length of σ -conjugation, and shifts to higher wavelengths until it reaches a maximum wavelength at $n = 20-24$ [8]. These transitions can be attributed to a transition between the σ and σ^* orbitals in the Si framework [8]. The alkyl-substituted polysilanes in solution display strong electronic transitions in the region of 300-310 nm, while the aryl-substituted polysilanes absorb in the region of 335-345 nm [8]. The red shift of 20-30 nm in the aryl derivatives is due to the interaction of the substituent π orbitals with the orbitals on the silicon backbone [4].

The absorption spectra of thin films are significantly different from the absorption spectra of solutions [10]. In cases where conformational rigidity is enforced by side-chain crystallization, the electronic absorption occurs at significantly longer wavelengths than expected [10]. In the case of thin films of poly(di-n-hexylsilane), the spectrum showed an intense absorption at 374 nm with a weak absorption at 317 nm [10]. Upon heating the film at 100°C, the absorption band at 374 nm shifted to 317 nm indicating that the n-hexyl side groups melted and introduced disorder into the backbone [10]. Upon cooling the film, the absorption band shifts back to 374 nm, indicating that the transition is fully reversible [10]. Transitions of this type can also be observed using DSC, IR and Raman and can be induced using pressure [9,10].

The polysilanes have also been found to be light sensitive both in solution and in solid form [4,8,11]. Upon irradiation, polysilanes degrade to lower molecular weight fragments [11]. Polysilanes with unsaturated pendent groups, such as poly(phenylmethylsilane), exhibit crosslinking in addition to degradation [11]. The photodegradation can be studied using ultraviolet spectroscopy. As the polymer degrades and the molecular weight decreases, the absorption band shifts to shorter wavelengths [11].

The unique properties of the polysilanes have led to a number of important applications. In the mid-1970's, Yajima and coworkers discovered that polydimethylsilane could be converted to the ceramic β -silicon carbide through a series of steps [12]. More recently, however, polysilane copolymers have been developed which can be directly converted to silicon carbide through the following reaction [13]:



The copolymer is synthesized using conventional techniques, melted and cast into the desired form and then crosslinked using ultraviolet light. The crosslinked polymer can then be converted to silicon carbide by heat-treatment. The main advantages of this technique are that the method is straightforward and ceramics can be produced which are uniform in shape and size [13,14].

Other possible applications include the use of polysilanes in microlithography [11,15], as semiconductors [16] and as photoinitiators for polymerization [17].

References

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