Preparation of Amphiphilic Polysilanes Bearing Chiral Pendant Ammonium Moieties

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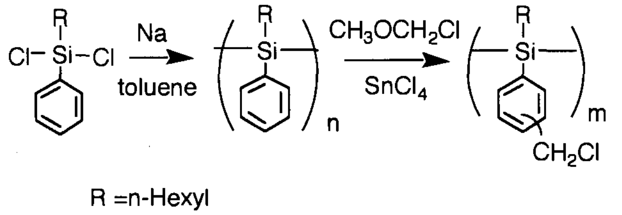
The synthesis and characterization of new amphiphilic polysilanes containing chiral pendant ammonium groups are described. Chloromethylation of polyhexylphenylsilane (PHPS) was carried out to give p-chloromethylated PHPS (**1**). **1** was treated with optically active N,N-dimethyl-α-methylbenzylamine to give an amphiphilic polysilane. The polymer prepared was soluble in water, ethanol and acetonitrile. The circular dichromic spectrum of the polymer in ethanol showed that the the polymer had a screw-sense main chain.

Polysilanes display unique characteristics such as UV absorption and luminescence, due to the σ-conjugation of the Si-Si main chain. It is important to control the conformation of the Si-Si main chain to develop application of the polysilanes for functional materials. Attention has been focused on the preparation and characterization of amphiphilic polysilanes carrying ether,[1] phenol,[2] and ammonium moieties[3] in the side chain, since they are expected to have potential for highly orientated structures of the polysilane main chain. For example, a unimolecular film prepared from the polysilane, which has phenol in the side chain by the Langmurie Blodgett method, showed clear anisotropy in its UV spectra.[2]

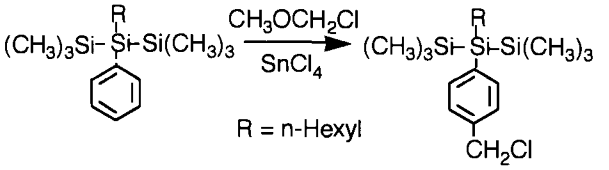
On the other hand, there are few reports on the preparation of polysilanes bearing asymmetric moieties.[4, 5] Fujiki reported that polysilanes bearing an optically active 2-methylbutyl group on silicon exhibited strong UV absorption and luminescence due to the screw-sense conformation of the main chain.[4] Most of the functionalized polysilanes, except for the ammonium functionalized one,[3] were prepared by the Wurtz reaction using dichlorosilane derivatives bearing optically active groups on silicon. In this method, however, the available asymmetric substituents are strictly limited, because they must be stable under the Wurtz coupling conditions. Introduction of functional groups to a preformed polysilane is another possibility to extend the method for the preparation of functionalized polysilanes.

In the course of our study on the synthesis and characterization of new polysilanes, an amphiphilic polysilane bearing chiral pendant ammonium moieties was investigated for the effects of the chiral moieties on the polysilane main chain.[6] Poly-n-hexylphenylsilane (**1**),[7] (Mw 1.5×10^5, Mw / Mn=2.10, polystyrene standard; UV absorption, λ_{max} 347 nm, ε 14400 in $CHCl_3$), was prepared by the Wurtz reaction under irradiation of supersonic waves in 22% yield. Friedel-Crafts chloromethylation using a tin tetrachloride catalyst was carried out to give the corresponding chloromethylated polysilane (**2**) in 90% yield (Scheme 1). Partial cleavage of the polysilane main chain was observed during the chloromethylation reaction,[8] and the average molecular weight decreased to 1×10^4 (Mw / Mn=1.65), which corresponds to about 42 silane units.[9] The ^{1}HNMR spectrum of **2** showed the chloromethylation was completed, and no cleavage, *ipso* -substitution, was observed between the Si-Ph bond.[10]



Scheme 1.

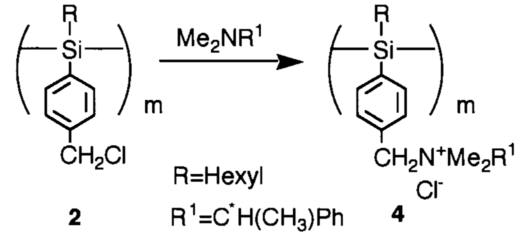
Because of the broad absorption, however, it was difficult to determine the position of the chloromethyl substituents on the aromatic rings. In order to investigate the positions and selectivities for the chloromethylation reaction, a model compound, 2-hexyl-1,1,1,3,3,3-hexamethyl-2-phenyltrisilane was chloromethylated in a similar manner to that described above (Scheme 2). The reaction gave only one chloro-methylated product, and its ^{1}HNMR spectrum[11] showed a typical AA'BB' pattern in the aromatic region corresponding to the *p*-substituent, although it was reported that chloro-methylation of trimethylsilylbenzene gave a mixture of *o*-, *m*-, and *p*-isomers.[12] It is understandable that the increased bulkiness of the substituent on silicon of the model compound compared with trimethylsilylbenzene forced the chloromethyl substituent to the *p*-position, selectively. These results let us to the conclusion that the chloromethyl substitution of **2** took place at the *p*-position to silicon.



Scheme 2.

Then **2** was treated with optically active N,N-dimethyl-α-methylbenzylamine (**3**).[13] A solution of **2** and (+)-**3** in toluene was kept at 80 ℃ for 12h to give the polysilane bearing optically active ammonium moieties ((+)-**4**) in 88 % yield (Scheme 3). The completion of the quarternization was confirmed by the disappearance of the chloromethyl peak (4.4 ppm) in the ^{1}HNMR spectrum of the product.[14] Compound **2** was also treated with (-)-**3** and (±)-**3** in a similar manner to that described above, to give (-)-**4** and (±)-**4**, respectively. The polysilanes obtained were white powders, and soluble in water, ethanol, and acetonitrile.

The UV spectrum of (+)-**4** showed an absorption due to Si-Si σ-bonds in the 320 to 355 nm region (λ_{max} 339 nm, ε 6800 in EtOH) (Figure 1). The CD spectrum of (+)-**4** showed negative



Scheme 3.

broad absorption (λ_{ext} 334 nm, $\Delta\varepsilon$ -0.72 (Si unit) in EtOH) in a similar region to the UV absorption and positive absorption based on aromatic groups. On the other hand, the CD spectrum of (-)-**4** exhibited a symmetrical pattern to that of (+)-**4** (λ_{ext} 336 nm, $\Delta\varepsilon$ 0.30 (Si unit) in EtOH) (Figure 2). No CD absorption was observed in the spectrum of (±)-**4** . These results suggest that the polysilane main chain of (+)-**4** and (-)-**4** have opposite one way screw-like conformation, altenately. In addition, it was found that the polysilane (+)-**4**, prepared from a 50 % chloromethylated **2** and (+)-**3**, gave nearly the same CD spectrum to that of the completely substituted (+)-**4** . It means that a half-percent of substituents adequately controls the polysilane main chain.[4]

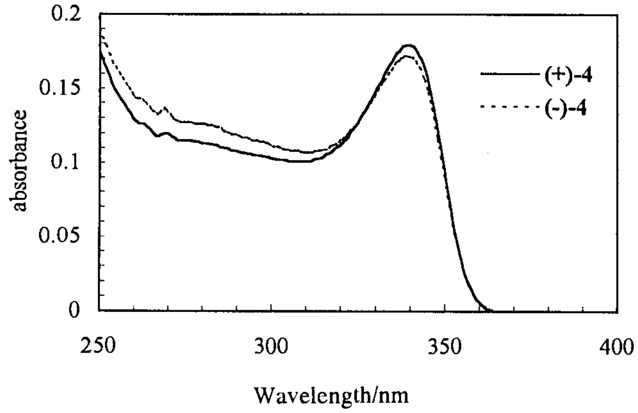


Figure 1. UV spectra of (+)-**4** and (-)-**4** in 99 % EtOH.

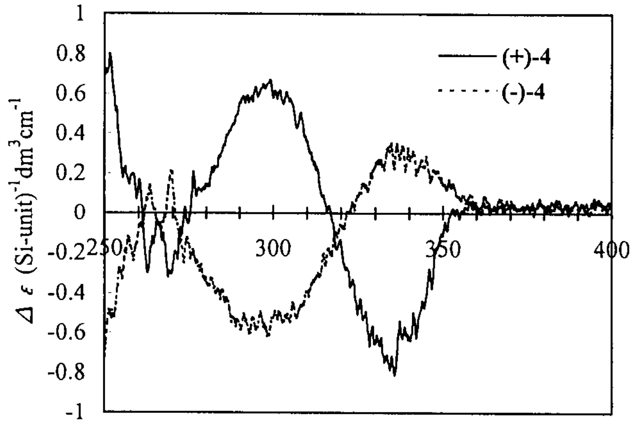


Figure 2. CD spectra of (+)-**4** and (-)-**4** in 99 % EtOH.

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9 Tin tetrachloride (1.0 g, 3.8 mmol) was added to a solution of **1** (1.0 g, 5.3 mmol) in chloroform (10 ml) at 0℃. The mixture was stirred at 0 ℃ for 6 h , and further 12 h at room temperature. After usual work-up, a white powder was obtained in 90% yield.

10 ^{1}HNMR (400MHz, $CDCl_3$), δ -0.5-1.5 (broad, 13H, C_6H_{13}), 4.4 (broad s, 2H, CH_2Cl), 6.0-7.4 (broad, 4H, Ar), UV absorption; λ_{max} 347 nm, ε 12600 ($CHCl_3$).

11 ^{1}HNMR (400MHz, $CDCl_3$), δ 0,14 (s, 18H, Si-CH_3), 0.88 (t, 3H, C-CH_3), 0.99-1.03 (m, 2H, Si-CH_2), 1.26-1.39 (m, 8H, CH_2), 4.52 (s, 2H, CH_2Cl), 7,31 (d, 2H, J=7.9Hz, Ar), 7.39 (d, 2H, J=7.9Hz, Ar).

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14 ^{1}HNMR(DMSO-d6, 400MHz): All the absorption were broad. δ 0-1.5 (13H, C_6H_{13}), 1.7-2.2 (3H, $NCCH_3$), 2.4-3.2 (6H, N^+CH_3), 4.0-5.0 (2H, N^+CH_2), 5.0-6.0 (1H, N^+CH), 7.0-8.1 (9H, Ar).