Remarkable effects of side-chain alkyl substituents on thermochromic behavior of peralkyldecasilanes

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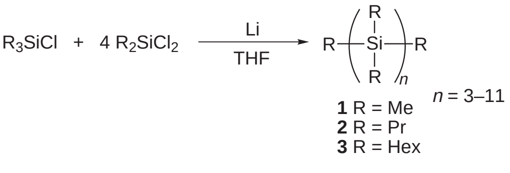
The absorption spectrum of perhexyldecasilane shows marked temperature dependence; a two-site model, similar to the transition from a random coil to an all pseudo-*trans* rod conformation proposed for poly(dihexylsilylene), is proposed to explain this effect.

Much attention has been focused on the remarkable thermochromism and unusual emission spectra of linear peralkylpolysilanes.[1] Typically, while poly(dihexylsilylene) exhibits a broad absorption band at *ca.* 315 nm at room temperature, upon cooling below *ca.* −30 °C, the absorption band becomes much narrower and shifts significantly to higher wavelength; the difference of $\lambda_{\max}$ between the low and high temperature regions ($\Delta\lambda_{\max}$) amounts 39 nm.[2a] The origin of the thermochromism is usually ascribed to the transition at low temperatures from a random coil to an all pseudo-*trans* rod conformation of the silicon backbone,[2] while Miller *et al.* have proposed that the red shift at low temperatures is caused by aggregation of polysilane chains.[3] In order to elucidate the origin of the thermochromism of the polysilanes, it is desirable to investigate peralkyloligosilanes with uniform Si chain lengths. However, there has been no study of peralkyloligosilanes other than permethyloligosilanes[4] reported until now, while we have recently reported circular dichroism (CD) spectral features of oligo(dipropylsilylene)s with terminal chiral aralkyl groups.[5] We report here that the absorption spectra of peralkyloligosilanes with ten or more Si atoms in a chain are remarkably temperature dependent, a feature which depends strongly on the side-chain alkyl substituents.

Wurtz coupling of a mixture of a dialkyldichlorosilane and a trialkylchlorosilane with lithium in THF gave a mixture of the corresponding peralkyloligosilanes, as shown in Scheme 1. Oligosilanes having 3–11 Si chains were separated as pure compounds *via* recycle HPLC from a mixture of peralkyloligosilanes. The structures were characterized by means of NMR spectroscopy, elemental analyses and mass spectrometry.‡

The absorption band maxima at 293 K and their dependence on the Si chain lengths of perpropyl- **2** and perhexyloligosilanes **3** were similar to those of permethyloligosilanes,[6] while small alkyl substituent effects were observed. These absorption bands are assigned to the σ→σ* electronic transitions of the Si main chains.[4,6]

Peralkyloligosilanes having more than five Si atoms in a chain showed significant red-shifts of the maxima with lowering temperatures. The most remarkable thermochromism was observed in perhexyloligosilanes with 10 and 11 Si atoms in the chain. Fig. 1 shows the temperature dependence of absorption spectra of peralkyldecasilanes **1a** (**1**, $n = 10$), **2a** (**2**, $n = 10$) and **3a** (**3**, $n = 10$). With lowering temperatures, the absorption maxima of these decasilanes shifted to longer wavelength, but the extent of the red-shift ($\Delta\lambda_{\max}$) from 293 to 77 K was markedly dependent on the substituents; $\Delta\lambda_{\max}$ values were < 10, 13 and 19 nm for **1a**, **2a** and **3a**, respectively; upon increasing the chain-length of the alkyl substituents, the thermochromic behavior of the decasilanes resembles more closely that of poly(dihexylsilylene). The temperature dependence of the absorption spectrum of **3a** was analyzed using a two-site model similar to the transition from random coil to the all pseudo-*trans* rod conformation model for poly(dihexylsilylene) (Scheme 2). Thus, a linear relationship was observed between $\log(A_1/A_2)$ and $1/T$, where A_1 and A_2 are the areas of the



Scheme 1

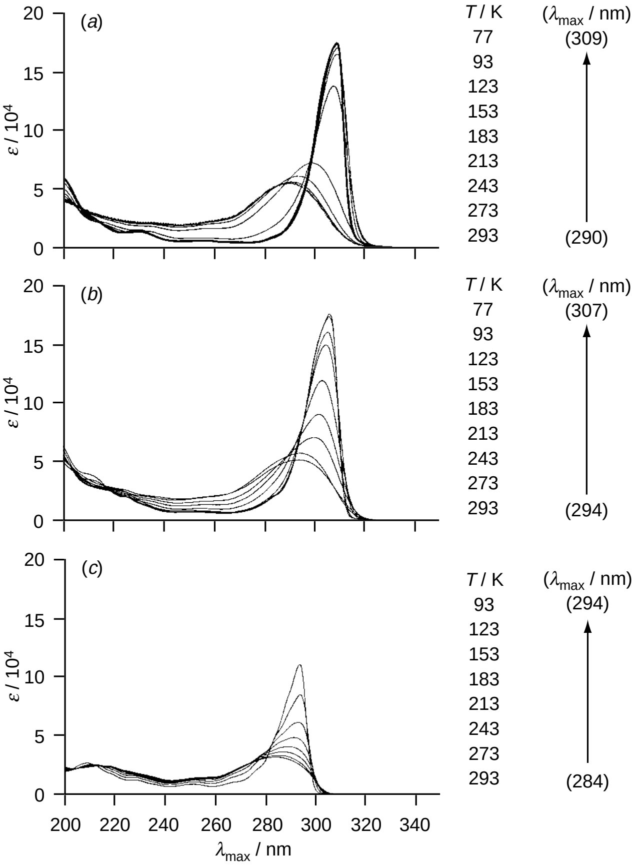


Fig. 1 Temperature dependence of absorption spectra of (*a*) docosahexyldecasilane **3a**, (*b*) docosapropyldecasilane **2a** and (*c*) docosamethyldecasilane **1a** in 3-methylpentane

$$\text{Site 1 (random coil)} \xrightleftharpoons{K} \text{Site 2 (all pseudo-}\textit{trans}\text{ rod)}$$

Scheme 2

absorptions bands at 290 and 310 nm for **3a**, respectively; the absorption spectra of **3a** were deconvoluted to the two bands by band-shape analysis. From the slope of the linear relationship, the enthalpy difference between the two sites was estimated to be 9 kcal mol^{-1}.

The remarkable effect of the substituents on the temperature dependence of the absorption spectrum of decasilane is ascribed to the importance of the steric energies between the side-chain alkyl substituents. MM2 force field calculations using standard parameters for organosilicon compounds proposed by Allinger[7] showed that the most stable conformation of **1a**–**3a** was as loose helical rods having a dihedral angle of *ca.* 170° for seven Si tetrads, irrespective to the alkyl substituents; the all-*trans* rod structure (the dihedral angle = 180°) showed much higher steric energy due to the severe steric repulsion between alkyl groups in 1,3-positions. The energy differences between the loose helical rod conformation and the other conformations with one *gauche* arrangement in the 7 Si tetrads of a decasilane are 5.3 and 8.9 kcal mol^{-1} for **2a** and **3a**, respectively; this value is much smaller for **1a** (0.5 kcal mol^{-1}). A one-*gauche* conformation in **3a** or **2a** causes severe steric repulsion between alkyl substituents, while the repulsion is less important in **1a**. The steric energy calculated by the MM2 method is in good agreement with the experimental ΔH values for the transition from Site 1 to Site 2, suggesting that the transition occurs between an assembly of conformations with one or more *gauche* Si tetrads to an assembly of all pseudo-*trans* rod conformations including a loose helical conformation.

Notes and References

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‡ *Selected data* for **2a**: 0.3% yield (based on Pr_2SiCl_2); a white powder; δ_H(300 MHz, C_6D_6) 0.65–1.05 (m, 44 H), 1.10–1.28 (m, 66 H), 1.60–1.80 (m, 44 H); δ_C(75 MHz, C_6D_6) 16.8, 17.4, 17.66, 17.67, 17.8, 18.8, 18.9, 18.97, 19.00, 19.04, 20.9, 21.0; several peaks overlap. The ^{29}Si NMR spectrum of **2a** was not measured due to poor sample solubility. For **3a**: 0.5% yield (based on Hex_2SiCl_2); a colorless viscous oil; δ_H($CDCl_3$) 0.63–0.75 (m, 32 H), 0.79–0.94 (m, 78 H), 1.20–1.44 (m, 176 H); δ_C($CDCl_3$) 13.79, 14.13, 14.44, 14.64, 14.91, 14.96, 22.74, 22.83, 22.87, 25.06, 27.16, 27.43, 27.51, 33.98, 34.17, 34.38, 34.40, 31.63, 31.82, 31.86; δ_{Si}($CDCl_3$) −33.82, −27.92, −26.18, −25.84, −10.12.

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