

Synthesis and Unusual Spectral Properties of (Alkoxycarbonyl)methyl-Substituted Polysilanes

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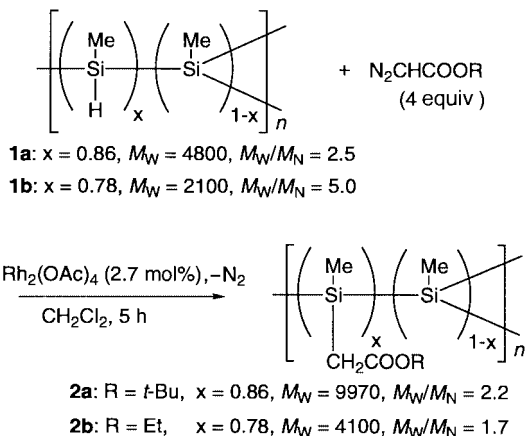
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UV-vis spectra of partially branched polysilanes having (alkoxycarbonyl)methyl substituents exhibit unusual spectral properties such as absorption of very long wavelength and temperature- and solvent-dependent change of the spectra. These observations suggest that polar substituents effectively promote the σ -conjugation of the silicon backbones.

σ -Conjugated polymers such as polysilanes and polycarbosilanes are attracting attention as materials with unique electronic and optical properties.¹ The electronic structures of silicon polymers are extremely sensitive to the nature of the substituents on the silicon.¹ However, little is known about the electronic effects of polar substituents, because of the difficulty of the synthesis of polysilanes having polar functional groups.² Recently, we have reported that introduction of amide groups into oligosilanes leads to a remarkable change of the $\sigma_{\text{SiSi}} \rightarrow \sigma^*_{\text{SiSi}}$ excitation energies.³ This observation has given an impetus to the studies of highly functionalized polysilanes. We describe here the synthesis and spectral properties of polysilanes **2** having (alkoxycarbonyl)-methyl substituents.



Functionalized polysilane **2a** was synthesized by the Rh-catalyzed carbenoid insertion⁴ into the Si-H bonds of partially branched poly(methylsilylene) **1a** containing 14% methylsilylene (MeSi) moieties ($M_W = 4800$, $M_W/M_N = 2.5$).⁵ To a solution of **1a** (486 mg) and $[(\text{CH}_3\text{CO}_2)_2\text{Rh}]_2$ (135 mg, 0.30 mmol) in dichloromethane (9.0 mL) was slowly added *tert*-butyl diazoacetate (6.3 g, 44 mmol) over a period of 5 h at room temperature. After concentration of the reaction mixture, resulting polymer was purified by GPC (toluene as eluent) to give 813 mg of partially branched polysilane **2a** having $\text{CH}_2\text{CO}_2t\text{-Bu}$ substituents as an air-stable yellow solid.⁶ Analysis of **2a** by GPC using polystyrene standards indicated that M_W was 9970 and polydispersity (M_W/M_N) was 2.2. Functionalized polysilane **2a** was soluble in

toluene, methanol and chloroform, and moderately soluble in isooctane. The ^{29}Si NMR spectrum of **2a** in C_6D_6 displayed two broad peaks at -35 ppm and -70 ppm, which are assignable to the silylene ($\text{MeSiCH}_2\text{CO}_2t\text{-Bu}$) and the silyne (MeSi) moieties, respectively.⁷ ^1H NMR spectroscopy also supported the polysilyne-polysilylene network structure containing 14% methylsilylene branching moieties, revealing that almost all the Si-H bonds of **1a** were converted to $\text{Si-CH}_2\text{CO}_2t\text{-Bu}$ moieties. Under the similar conditions, partially branched polysilane **2b** having $\text{CH}_2\text{CO}_2\text{Et}$ substituents ($M_W = 4100$; $M_W/M_N = 1.7$; 22% branching) was prepared from **1b** ($M_W = 2100$; $M_W/M_N = 5.0$) and ethyl diazoacetate.⁶

The solid state UV-vis spectra of a thin film of **2a** ($4.5 \mu\text{m}$ thick) are shown in Figure 1, where the spectrum of a thin film of *n*-octyl-substituted polysilane with same degree of branching, $[(\text{CH}_3\text{Si})_{0.14}(\text{n-C}_8\text{H}_{17}\text{SiCH}_3)_{0.86}]_n$ **3** ($M_W = 7780$; $M_W/M_N = 2.0$), is also given for comparison ($4.9 \mu\text{m}$ thick). The spectrum of **2a** at 25°C exhibited a monotonously decreasing broad band and a shoulder peak around 300 nm , which is assignable to $\sigma_{\text{SiSi}} \rightarrow \sigma^*_{\text{SiSi}}$ transition of the linear silylene moieties.¹ Both spectra of **2a** and **3** display similar featureless broad bands, which are characteristic of branched polysilanes.⁸ However, functionalized polysilane **2a** showed broader absorption extending to the visible region ($\leq 480 \text{ nm}$), while *n*-octyl-substituted polysilane **3** exhibited absorption in the near UV region ($\leq 350 \text{ nm}$).⁹ The remarkable red-shift of the absorption edge of **2a** relative to **3** apparently indicates that the $\text{CH}_2\text{CO}_2t\text{-Bu}$ substituents in **2a** effectively promote the σ -conjugation and hence reduce the band gap (E_g) from 3.54 eV to 2.58 eV .¹⁰

The spectrum of the thin film of **2** displayed a reversible temperature-dependent change. For example, when the film of

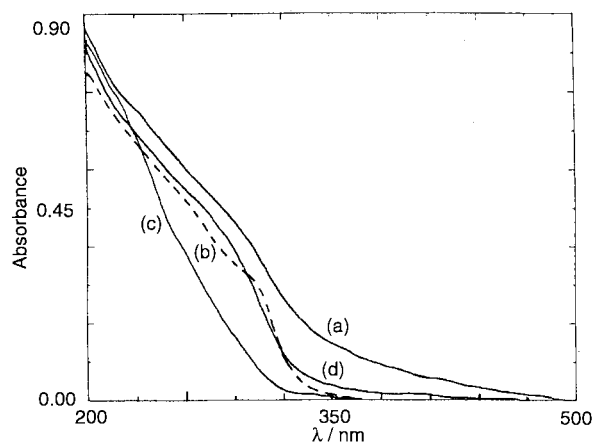


Figure 1. UV-vis spectra of (a) thin film of **2a** at 25°C , (b) thin film of **3** at 25°C , (c) thin film of **2a** at 100°C , and (d) thin film of **2a**, heated at 100°C and cooled at 25°C for 2 h.

2a was heated at 100 °C for 15 min, the absorption edge significantly blue-shifted from 480 nm to 350 nm (Figure 1 (c)). This absorption, however, was not retained upon cooling at room temperature and the spectrum (a) slowly returned after 5 h via transient spectrum (d). The thermochromic behavior of **2a** can be explained by assuming that the blue-shift of the absorption edge at 100 °C is caused by thermally induced conformational change of the silyne moieties,¹¹ since the long-wavelength absorption above 400 nm is attributable to the silyne moieties.¹² This assumption can be sharply contrasted with the fact that conformationally rigid polysilynes substituted with alkyl groups do not display thermochromic change of the absorption spectra.¹³ Thus, it seems likely that the $\text{CH}_2\text{CO}_2t\text{-Bu}$ substituent exerts a strong influence on the conformation of the silyne moieties, although the group is bonded to the silylene moieties.¹⁴

The hypothesis is strengthened by the solvent-dependent change of the solution spectra of **2a**. In aqueous methanol solution, **2a** exhibited broad absorption extending to 485 nm, which is essentially similar to the solid-state spectrum (Figure 2 (a)). The intensities of the absorbance at 350 and 440 nm are 1289 and $352 \text{ M}^{-1}\text{cm}^{-1}$ per Si–Si bond, respectively. In contrast, in nonpolar solvent such as isooctane, the long-wavelength absorption completely disappeared (Figure 2 (b)).¹⁵ The solvatochromic change of the spectra strongly suggests that conformational change of the silyne moieties is responsible for the disappearance of the long-wavelength absorption, since the absorption above 400 nm possibly arises from the silyne moieties of **2a**.¹²

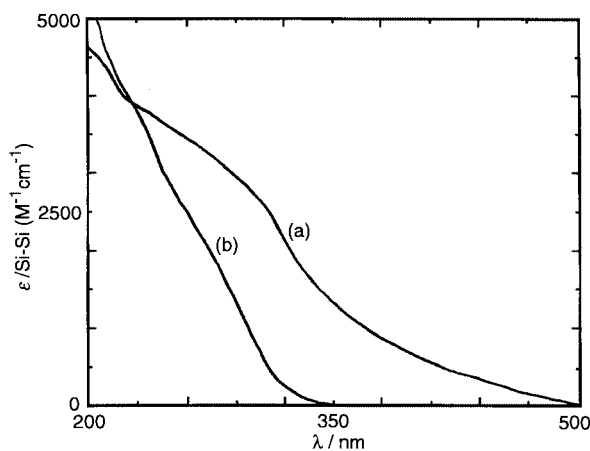


Figure 2. UV-vis spectra of (a) **2a** in aqueous methanol ($\text{MeOH:H}_2\text{O} = 500 : 1$) and (b) **2a** in isooctane.

Therefore, it is reasonable to consider that the polar $\text{CH}_2\text{CO}_2\text{R}$ substituents effectively promote the σ -conjugation along the silicon backbone through the conformational control of the backbone.¹⁶ The origin of this remarkable promotion of σ -conjugation by polar substituents is not clear. The polarizability of the silicon chains is supposed to increase with increasing σ -conjugation length along the silicon chains.¹⁷ Thus, stabilization of delocalized electronic state of the polysilanes can occur via electrostatic, dipole-dipole interaction between the polar ester groups and highly polarizable silicon chains, promoting the σ -conjugation in the solid state.¹⁷ The $\text{CH}_2\text{CO}_2\text{R}$ substituents in **2** would stabilize the backbone conformations that allow the effective electron delocalization, whereas conformational change at high temperatures leads to

the blue-shift of the absorption edge. The solvatochromic behavior of **2a** is also consistent with this proposal; in highly polar aqueous methanol, strong electrostatic interaction between the solvent molecules and polarizable silicon chains should greatly promotes the σ -conjugation.

In conclusion, we have shown that functionalization of the partially branched polysilanes with ester groups effectively reduces the $\sigma_{\text{SiSi}} \rightarrow \sigma_{\text{SiSi}}^*$ excitation energies via the conformational control of the silicon backbones.

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References and Notes

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