A Statistical Model for the Cooperative Thermochromic Transition of Polysilanes[1]

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ABSTRACT: A statistical model for the cooperative thermochromic transition of polysilanes is proposed. The basic assumption of this treatment is that the origin of the thermochromism is the conformational transition between two ordered states, i.e., all-trans and helix structures. We have calculated the partition function of a single polysilane chain by assuming that the total conformational energy of the chain can be described by a simple sum of the nearest-neighbor interaction energies and the energies of trans, gauche(+), and gauche(−) structures. A comparison of the theoretical results with the experimental intensity of absorption maxima has enabled us to estimate the free energy of stabilization of the ordered sequences. The calculation suggests that the transition-type thermochromism is observable only when the conformational stabilization energies of the ordered sequences are large.

Introduction

Polydiacetylenes,[2] and polythiophenes[3] (a class of π-conjugated polymers), and polysilanes[4] (a relatively new class of σ-conjugated polymers) exhibit an intense electronic absorption band in the ultraviolet region, which has been attributed to extensive delocalization of electrons along the main chain. The electronic properties of these conjugated polymers are largely dependent on the conformation of the polymer chain. One of the most exotic properties of these polymers is their thermochromism, which must be the key phenomenon in understanding the correlation between the electronic and conformational properties.[5]

Among polysilanes, poly(di-*n*-alkylsilane)s exhibit a variety of interesting thermochromic behaviors that depend on the nature of the alkyl substituents.[6] As temperature decreases, polysilanes undergo either a gradual or an abrupt shift of the absorption band to longer wavelengths. A well-studied example of the latter type is poly(di-*n*-hexylsilane), which undergoes a transition at ca. −30 °C in hexane, with a UV absorption shift of $\lambda_{\max}$ from 314 to 354 nm. The thermochromism of polysilanes has been extensively studied and considerable effort has been devoted to elucidating the nature of the thermochromic transition.[7] Some progress has been made toward understanding why thermochromism is accompanied by an abrupt absorption shift. Zeigler and Harrah have proposed a rod-to-coil transition model,[6b] which closely resembles the helix-coil transitions of biopolymers.[8] The low-energy absorption maximum has been ascribed to that of the rod form, which is assigned to the absorption of the low-temperature all-trans form. The absorption maximum of the high-temperature form, however, lies at a longer wavelength than that of unsymmetrically dialkyl-substituted polysilanes such as poly(*n*-hexylmethylsilane).[6a] Moreover, the amount of temperature-induced shift of the absorption maximum for the high-temperature form of symmetrically substituted poly(dialkylsilane) is generally very small. These results cast some doubt on the assumption that the high-temperature form is the coiled state. Indeed, recent investigations have shown that the high-temperature form is far from the coiled state; rather, indications are that it is a helical-rod form with relatively long persistence length.[9]

The only theoretical attempt to understand this interesting behavior may be the treatment by Schweizer.[10] He proposed that such a transition could be "polarization driven" and is possibly due to polymer−solvent induced-dipole van der Waals interactions caused by the large increase in the polymer polarizability resulting from conformational changes to the more extended "all-trans" conformation. Thus he attempted to explain qualitatively the nature of the thermochromism of polydiacetylenes and polysilanes. Energetic consideration is based on the independent effect of gauche bonds in the polysilane case, which are randomly introduced on the main chain. The conjugation length was estimated by minimizing the free energy of a single polymer chain as a function of the defect concentration. Some relevant work has been reported to support the proposal.[11] This is somewhat different from the usual statistical treatments of the helix-coil transition, because the conjugation length is usually calculated directly from the partition function without any a priori assumptions on the distribution of the defects. A comparison between this theory and experiment has not been made, and the general features of the transition could not be reproduced. However, the polarization of the delocalized electrons by the solvent molecules cannot be the principal energetic reason for the transition, at least not for the polysilanes. For example, although the attractive interactions between the more extended trans form and the solvent should be expected to induce the solubilization of the polymer around the transition temperature, precipitation of polymer in the vicinity of the transition temperature is observed.[6a]

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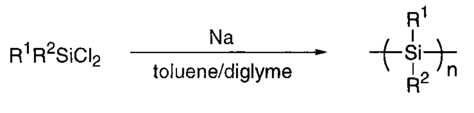
Table 1. Molecular Weights and Polydispersities of Polysilanes


$$R^1R^2SiCl_2 \xrightarrow[\text{toluene/diglyme}]{\text{Na}} -\!\!(\text{Si}(R^1)(R^2))\!\!-_n$$

R^1, R^2	M_n[a]	M_w/M_n[a]
hex, hex	2.9×10^5	1.9
hex, pr	3.8×10^5	1.9
hex, Me	6.3×10^4	2.3

[a] Determined by GPC with polystyrene standards.

Several important results have been reported concerning the behavior of poly(di-*n*-hexylsilane) in dilute solution. The conformation of the polymer around room temperature is found to be rodlike, with a persistence length of 60−70 Å, which consists of a certain ordered form. Moreover, the radius of the polymer coil decreases sharply below the transition temperature, which strongly indicates that the transition is caused unimolecularly in the very dilute solutions. Thus, it appears that the abrupt transition around −30 °C for poly(di-*n*-hexylsilane) in solution is essentially induced by the conformational change of a single molecule, although the overall behavior of the transition is not obvious. This observation encouraged us to treat the transition theoretically as a cooperative phenomenon based on a simple statistical model.

In this paper, we present a simple theory that takes into account the phenomenological electronic and conformational coupling effect of the σ-conjugated polymer chain as well as the conformational changes of the individual polymer units. In view of the fact that the transition is accompanied by an overall structural change of the polymer chain, the free energy change of the chain disordering was taken into account as the principal cause of the chain disordering, a process that should occur cooperatively. The basic assumption of this treatment is that the origin of the thermochromism is the conformational transition between two ordered states. A comparison of the theory with the intensity of the absorption maxima enables us to estimate the free energies of stabilization of trans and gauche sequences. Some results on the temperature dependence of the sequence distributions are also given.

Results and Discussion

Preparation of Poly(di-*n*-alkylsilane). Poly(di-*n*-hexylsilane), poly(*n*-hexyl-*n*-propylsilane), and poly(*n*-hexylmethylsilane), which exhibit the characteristic thermochromic behavior, were prepared in the usual manner by reductive condensation of the corresponding dichlorosilane with sodium metal.[12] The molecular weights and polydispersities of these polysilanes are listed in Table 1. The molecular weights are so large that the thermochromic behavior of these polysilanes should be independent of the molecular weight.[13]

Thermochromic Behavior of Poly(di-*n*-alkylsilane) in Solution. The temperature-dependent UV spectra of poly(di-*n*-alkylsilane) were measured in dilute hexane solution. Figure 1 shows the thermochromic behavior of poly(di-*n*-hexylsilane), poly(*n*-hexyl-*n*-propylsilane), and poly(*n*-hexylmethylsilane). As shown in the UV spectra, the thermochromic behavior has been divided into three categories with respect to the substituent groups of the polysilanes, similar to those observed previously.[6]

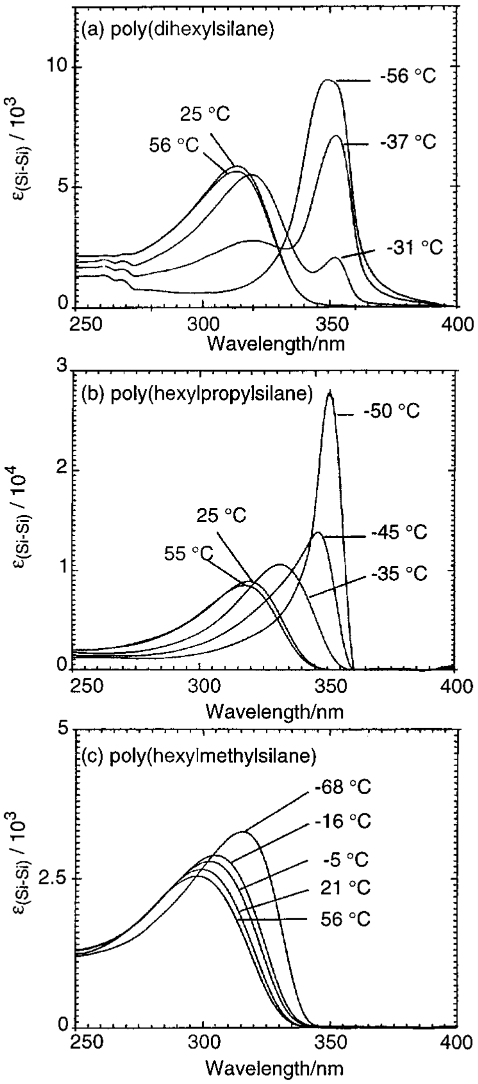


Figure 1. Temperature-dependent UV spectra of poly(di-*n*-alkylsilane) in hexane: (a) poly(di-*n*-hexylsilane), (b) poly(*n*-hexyl-*n*-propylsilane), and (c) poly(*n*-hexylmethylsilane).

The first and most interesting group consists of the symmetrically substituted polysilanes with long alkyl substituents such as poly(di-*n*-hexylsilane). The absorption maximum observed for this group of polymers at around room temperature disappeared and a new band was generated at a longer wavelength at temperatures below −30 °C, as shown in Figure 1a. In addition, the range of the transition temperature was very narrow. This type of thermochromism is called the transition type here.

The second group is represented by poly(*n*-hexyl-*n*-propylsilane), in which the absorption maximum shows a gradual bathochromic shift accompanied by a significant increase of the absorption intensities with decreasing temperature, as shown in Figure 1b. This type is called the intermediate type here.

The third type of behavior is exemplified by spectra of the highly unsymmetrical polysilanes such as poly(*n*-hexylmethylsilane), as shown in Figure 1c. The absorption maximum of poly(*n*-hexylmethylsilane) undergoes a continuous bathochromic shift with decreasing temperature. This type is called the nontransition type here.

Statistical Model for the Cooperative Thermochromic Transition of Polysilanes. The thermochro-

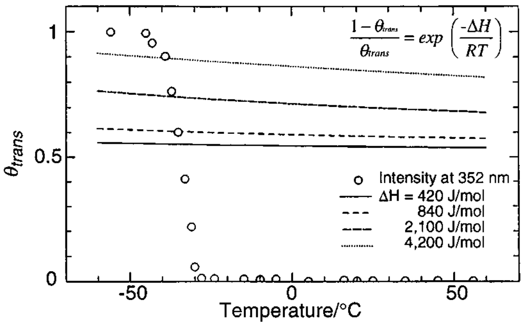


Figure 2. Independent conformational changes of the trans and gauche units of poly(di-*n*-hexylsilane) calculated based on the Boltzmann distribution, where θ_{trans} was assumed to be proportional to the absorption intensity at 352 nm.

mic behavior of the transition type as observed for poly(di-*n*-hexylsilane) is the most interesting one. This unique behavior is thought to be caused by the conformational change of the polysilane main chain, where the absorption at 360 nm could be assigned to the all-trans form.[14]

However, such an abrupt transition is very difficult to interpret in terms of the independent conformational changes of trans or gauche units of the silicon−silicon single bond of the main chain on the basis of the Boltzmann distribution.[15] The absorption intensities at 352 nm corresponding to the trans units are plotted in Figure 2 as a function of the temperature for poly(di-*n*-hexylsilane) in hexane. The absorption intensities increase sharply at temperatures below −30 °C. Calculated lines based on an independent Boltzmann distribution with the conformational energy differences between trans and gauche units, ΔH, are also plotted in Figure 2. Here the trans fraction was assumed to be proportional to the absorption intensity at 352 nm. The conformational changes of this polysilane cannot be explained on the basis of an independent conformational population of trans and gauche units. Therefore, some kind of cooperation should be associated with the conformational transition for the transition-type thermochromism. Then the transition process can be analyzed as a cooperative interconversion between two well-defined states, not via an intermediate state composed of a mixture of trans and gauche units.

Several basic assumptions were made before going into the theoretical consideration of the cooperative nature of the conformational transition for the transition-type thermochromism. Our basic assumptions are as follows: First, at low temperature, polysilane takes a planar, all-trans-ordered conformation. With increasing temperature, the all-trans conformation changes abruptly to another well-defined form. The latter may be regarded as a helix-ordered conformation because the absorption maximum of poly(di-*n*-hexylsilane) in hexane solution is very close to that observed for the solid film at high temperature, which was suggested to be a $^7/_3$ helical conformation as determined by both polarizing optical microscopy and X-ray diffraction.[12] In this sense, the transition is not an order−disorder type but may be regarded as a transition between two ordered states. Indeed, we have recently found a clear isosbestic point for the temperature-dependent UV spectra of the solid film of poly(di-*n*-hexylsilane) during the thermochromic transition.[16] Second, it is assumed that the ordered helix form is transformed to a statistical mixture of trans and gauche units at high temperature. This assumption is introduced by the experimental facts of a recent publication, which show that the radius of gyration of the helix-rodlike form decreases with increasing temperature.[9] It is pertinent to note here that the detailed thermochromic behavior of poly(*n*-butyl-*n*-hexylsilane) in the solid state, involving not only all-trans and $^7/_3$ helix forms but also intermediate forms, has recently been reported.[17]

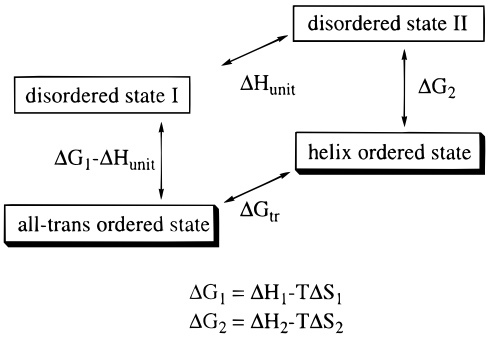


Figure 3. Schematic representation of the thermodynamics of the cooperative transition of polysilanes. ΔH_{unit} is difference of the conformational energy between single gauche and trans units. ΔG_1 and ΔG_2 are the free energies for the stabilization of helix and all-trans ordered states, respectively.

Table 2. Statistical Weight of *i*th and (*i* + 1)th Units with Nearest-Neighbor Interactions

i^{i+1}	t	g^+	g^-
t	1	1	1
g^+	ξ	η	0
g^-	ξ	0	η

The transition model for the polysilanes around the transition temperature is schematically shown in Figure 3. Here, ΔH_{unit} is the difference of the conformational energy between single silicon−silicon bond units. According to the standard procedure of the rotational isomeric model,[18] the conformational energy profile of polysilanes is represented by a 3-fold energy minimum, i.e., trans (t), gauche(+) (g^+), and gauche(−) (g^-). The transition process must be analyzed as a cooperative interconversion between two well-defined states, not via an intermediate state composed of a mixture of trans and gauche units. The direct transition from the all-*trans*-ordered state to the helix-ordered state is impossible, and the transition proceeds via the hypothetical disordered I and II states. For this model, the statistical weight of the *i*th and (*i* + 1)th units with nearest-neighbor interactions (ξ and η) are conveniently represented in the usual manner as shown in Table 2, a process similar to the one-dimensional Ising lattice.[19] ΔG_1 and ΔG_2 are the free energies of stabilization for the helix and all-trans states, respectively, as compared with the disordered II state.

Here ξ and η are represented by

$$\xi = \exp\{-(\Delta H_{\text{unit}} + \Delta G_1)/RT\} \tag{1}$$

$$\eta = \exp\{-(\Delta H_{\text{unit}} + \Delta G_1 - \Delta G_2)/RT\} \tag{2}$$

Then, the statistical weight matrix U is represented by

$$\boldsymbol{U} = \begin{pmatrix} 1 & 1 & 1 \\ \xi & \eta & 0 \\ \xi & 0 & \eta \end{pmatrix} \tag{3}$$

The partition function *Z(N)* of a polysilane chain is given by

$$Z(N) = \boldsymbol{e}U\boldsymbol{e}' \tag{4}$$

where unit vectors $\boldsymbol{e}$ and $\boldsymbol{e}'$ are

$$\boldsymbol{e} = (1\ 1\ 1), \quad \boldsymbol{e}' = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \tag{5}$$

and *N* is the number of monomer units on a polymer chain. Three eigenvalues of this matrix are

$$\lambda_{0,1} = \frac{1 + \eta \pm \sqrt{(1-\eta)^2 - 8\xi}}{2} \tag{6}$$

$$\lambda_2 = \eta \tag{7}$$

where λ_0 is the largest eigenvalue and the relationship $\lambda_1 \leq \lambda_2 \leq \lambda_0$ holds. Then, the fraction of gauche units (θ_g) is calculated, assuming that *N* is very large, by

$$\theta_g = \frac{1}{2}\left\{\frac{\eta - 1}{\sqrt{(\eta-1)^2 + 8\xi}} + 1\right\} \tag{8}$$

Because ΔG_1 and ΔG_2 are functions of temperature, we can determine the thermodynamic quantities of the thermochromic transition if we know the temperature dependence of the gauche quantity θ_g. The parameters selected were ΔH_1, ΔH_2, ΔS_1, and ΔS_2, which are the enthalpies and the entropies corresponding to ΔG_1 and ΔG_2, respectively. Note that only three of these parameters are independent because the difference between ΔG_1 and ΔG_2 is the free energy of transition, which can easily be determined at the midpoint temperature of the transition.

In addition, all statistical thermodynamic quantities of a single polysilane chain can be calculated if the partition function *Z(N)* is determined. Here the fraction of the trans and gauche units is rewritten by the eigenvalues

$$\theta_t = \frac{1 - \lambda_1}{\lambda_0 - \lambda_1} \tag{9}$$

$$\theta_g = \frac{\lambda_0 - 1}{\lambda_0 - \lambda_1} \tag{10}$$

Then, the averaged trans and gauche sequence lengths are calculated by

$$\langle N_t \rangle = \frac{\lambda_0}{\lambda_0 - 1} \tag{11}$$

$$\langle N_g \rangle = \frac{\lambda_0}{\lambda_0 - \eta} \tag{12}$$

Probabilities that *i*th to $(i + n - 1)$th bonds are also calculated by

$$p(i,nt) = \left(\frac{1}{\lambda_0^{\,n-1}}\right)\frac{1 - \lambda_1}{\lambda_0 - \lambda_1} \tag{13}$$

$$p(i,ng) = \left(\frac{\lambda_0 + \lambda_1 + 1}{\lambda_0}\right)\frac{\lambda_1 - 1}{\lambda_1 - \lambda_0} \tag{14}$$

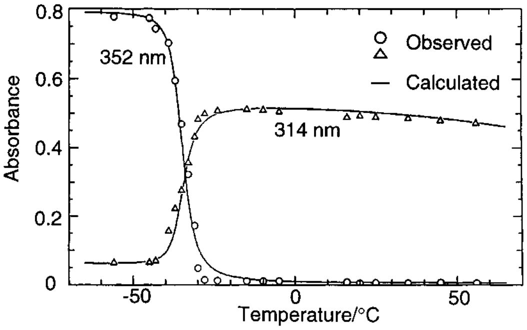


Figure 4. Observed and calculated absorbance of poly(di-*n*-hexylsilane) corresponding to the trans and gauche sequences.

In the practical calculation, the probabilities *p(i, nt)* and *p(i, ng)* were assumed to be proportional to the absorption intensity at 352 and 314 nm, respectively.

Furthermore, if the partition function of the partial chain could be correlated to the absorption intensities and wavelength ($\lambda_{\max}$), the calculation of the absorption spectra and $\lambda_{\max}$ might be possible. Here the partition function of a partial chain with a sequence length *n* within an infinite polysilane chain is denoted by

$$\boldsymbol{Z}_p(n) = (1 - \lambda_1\ 1\ 1)\begin{pmatrix} 1 & 1 & 1 \\ \xi & \eta & 0 \\ \xi & 0 & \eta \end{pmatrix}^n \begin{pmatrix} 1 \\ (\lambda_0 - 1)/2 \\ (\lambda_0 - 1)/2 \end{pmatrix} \tag{15}$$

However, the direct calculation of $\boldsymbol{Z}_p(n)$ was impractical for large *n* because the calculation of matrixes of size $n \times 2n$ was too time-consuming. Therefore, the simulation of the spectra was carried out by the Monte Carlo method for 1000 samples, where the sequence length was assumed to be 30.[20] The spectral shape of all sequences was assumed to be Gaussian.

Conformational Transition Energies of the Transition- and Intermediate-Type Polysilane Calculated by the Cooperative Transition Model. The calculation of the conformational energy of poly(di-*n*-hexylsilane) based on the cooperative transition model was carried out using our experimental data. Figure 4 shows the results. Poly(di-*n*-hexylsilane) exhibited abrupt thermochromic behavior within a very narrow range of temperature, as shown in Figure 1a. The absorption intensities at 352 and 314 nm were assigned to the two ordered sequences of poly(di-*n*-hexylsilane), and the conformational energies of each sequence were optimized to reproduce the experimental absorption. The experimental points are the intensities of the absorption at 352 and 314 nm for poly(di-*n*-hexylsilane) in hexane. The transition was very sharp and the midpoint temperature at which fractions of the all-trans low-temperature form and the high-temperature form are equal was about −34.5 °C. Solid curves were calculated by the present statistical model, using the same parameters for each of these fractions, where the minimum conjugation length was assumed to be 10. The agreement between the experimental points and calculated curves is excellent. The slight decrease of helical fraction at high temperatures may be ascribed to the partial admixing of the gauche sequences by the energetically more stable trans units. The parameter values determined are $\Delta H_1 = 31$ kJ mol^{-1}, $\Delta H_2 = 30$ kJ mol^{-1}, $\Delta S_1 = 40$ J K^{-1} mol^{-1} and $\Delta S_2 = 34$ J K^{-1} mol^{-1}, respectively. It should be noticed that the stabilization enthalpies ΔH_1 and ΔH_2 of the ordered structures are very

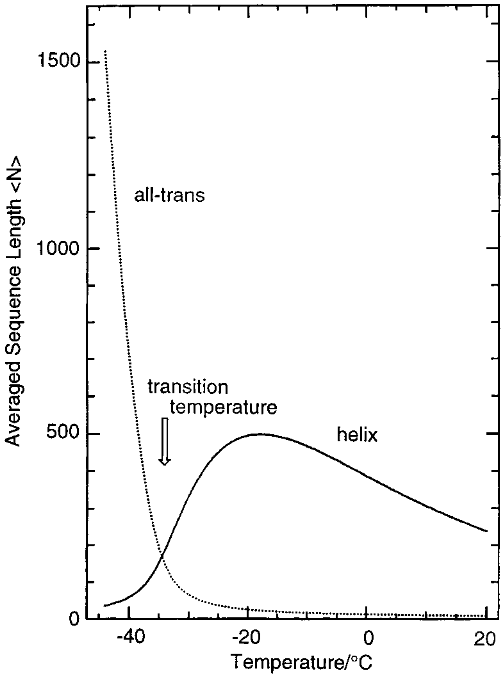


Figure 5. Calculation of the averaged trans and gauche sequence length of poly(di-*n*-hexylsilane) vs temperature.

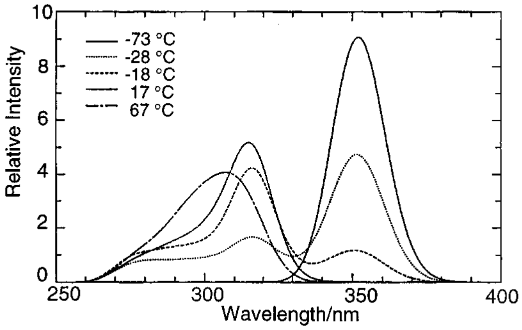


Figure 6. Simulation of the thermochromic behavior of poly(di-*n*-hexylsilane) by the Monte Carlo method.

large. These very large values of stabilization energies of the two ordered sequences must be dependent on the size of the alkyl substituents or on the sequence length of σ-conjugation or both.[13]

Figure 5 shows the calculated averaged length of the all-trans and helix sequence of poly(di-*n*-hexylsilane) plotted as a function of temperature. As shown in this figure, while the averaged length of the all-trans sequence denoted is almost 0 around room temperature, there is an immediate sharp increase at the temperature below -30 °C up to the all-trans sequence length of 10^3 at -40 °C. On the other hand, there is an immediate sharp decrease of the averaged length of the helix sequence at temperatures from below -30 °C to 0. The averaged length of the helix sequence gradually decreases above room temperature as the helix-ordered structure is finally transformed to the statistical mixture of the trans and gauche units at high temperature.

Figure 6 shows the spectral simulation of the thermochromic behavior for poly(di-*n*-hexylsilane) calculated by the Monte Carlo method, where ΔH_{unit}, and ΔH_1, and ΔH_2 are 2.5, 31, and 30 kJ mol^{-1}, respectively. The ΔH_{unit} value was selected by the analysis of the nontransition-type thermochromic behavior of poly(*n*-hexylmethylsilane) described below. The simulation could reproduce the sharp change of the experimental absorptions at 350 and 314 nm, which occurred within a very narrow range of temperature.

On the other hand, poly(*n*-hexyl-*n*-propylsilane) exhibited thermochromic behavior of the intermediate type, as shown in Figure 1b, in which the absorption maximum shows a gradual bathochromic shift accompanied by a significant increase of the absorption intensity with decreasing temperature. Therefore, the conformational stabilization enthalpies are expected to be small for this type of polysilane as compared with poly(di-*n*-hexylsilane). The conformational energies of poly(*n*-hexyl-*n*-propylsilane) were calculated by the same method as detailed above. The values of the conformational stabilization enthalpies are determined as $\Delta H_1 = 15$ and $\Delta H_2 = 13$ kJ mol^{-1}. The values for poly(*n*-hexyl-*n*-propylsilane) are about half those for poly(di-*n*-hexylsilane).

It should be noted that tacticity of the asymmetric polysilanes has not been considered. Since tacticity plays an important role for conformational states of the polymer, the thermochromic behavior of the asymmetric polysilanes should be influenced. However, tacticity-controlled polysilanes have not been synthesized. Therefore, at the present stage the conformational energies were fitted to the experimental data based solely on the statistical model. If the conformational analysis of the asymmetric polysilanes could be made, thermochromic behavior of the polysilanes would be identified.

A Statistical Model for the Conformational Change of the Nontransition-Type Polysilane. The conformational stabilization enthalpies are expected to be small for the unsymmetrically substituted polysilanes, such as poly(*n*-hexylmethylsilane),[21] because they do not show the transition-type thermochromic behavior in solution and the absorption maximum steadily shifts to higher wavelength without changing significantly the absorption intensity, as shown in Figure 1c. Therefore, no cooperative conformational change should exist, and the bathochromic shift has been explained by an increase in the low-energy trans units on the polymer chain with decreasing temperature.

In this case, the conformational energy of poly(*n*-hexylmethylsilane) was calculated on the basis of the independent transition of the trans and gauche units. Here, several assumptions are proposed: (1) independent transition occurs between the trans and gauche units, (2) absorption wavelength maxima (λ_{max}) changes linearly with the trans population, and (3) λ_{max} takes a minimum value (λ_{mix}) when the trans and gauche partitions are equal.

Then, the absorption wavelength maxima (λ_{max}) is represented by

$$\lambda_{\text{max}} = \lambda_{mix} + (2\theta_t - 1)(\lambda_{trans} - \lambda_{mix}) \qquad (16)$$

where λ_{trans} is 352 nm, on the basis of the absorption maximum of all-trans poly(di-*n*-hexylsilane) at a low temperature. The trans population (θ_t) is described by the following equation, assuming a Boltzmann distribution:

$$\frac{1 - \theta_t}{\theta_t} = \exp\left(-\frac{\Delta H_{\text{unit}}}{RT}\right) \qquad (17)$$

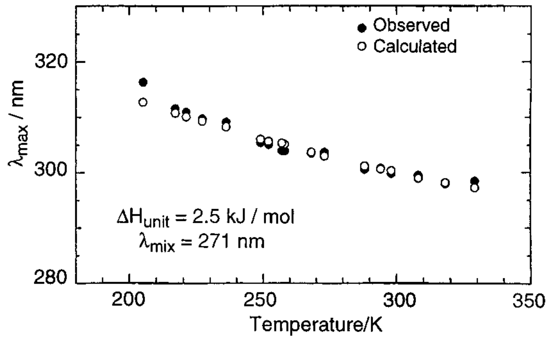


Figure 7. Plots of observed and calculated values of the temperature dependence of the absorption maxima of poly(*n*-hexylmethylsilane) in hexane.

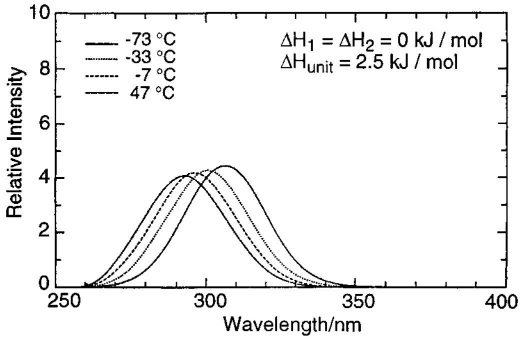


Figure 8. Simulation of the thermochromic behavior of poly(*n*-hexylmethylsilane) by the Monte Carlo method.

Therefore, λ_{max} can be represented by

$$\lambda_{max} = \lambda_{trans} - \frac{2(\lambda_{trans} - \lambda_{mix})}{1 + \exp\left(-\frac{\Delta H_{unit}}{RT}\right)} \tag{18}$$

The calculation was carried out by the Monte Carlo method by taking ΔH_{unit} and λ_{mix} as parameters. The result is shown in Figure 7, which demonstrates that the calculated points are in good agreement with the experimental points. The best-fit parameters are 2.5 kJ mol^{-1} and 271 nm for ΔH_{unit} and λ_{mix}, respectively.

Figure 8 shows the simulation of the thermochromic behavior of poly(*n*-hexylmethylsilane) by the Monte Carlo method, where ΔH_{unit} is 2.5 kJ mol^{-1} and ΔH_1 and ΔH_2 are 0 kJ mol^{-1}. The spectral simulation could reproduce well the experimental bathochromic shifts of the absorption maxima with decreasing temperature.

Alkyl Substituent Effects on the Thermochromism of Poly(di-*n*-alkylsilane). The effect of the alkyl substituents on the thermochromism of polysilanes has been satisfactorily explained by this model, on the basis of a cooperative transition. The energy difference between single trans and gauche units (ΔH_{unit}) was calculated to be 2.5 kJ mol^{-1} from the calculation of the nontransition type of polysilanes, as mentioned above. The intrinsic energy difference between single trans and gauche units of poly(di-*n*-alkylsilane) should be around this value. However, the thermochromic behavior of polysilanes is divided into three categories, depending on the nature of the alkyl substituent groups, i.e., transition, intermediate, and nontransition types. The type of thermochromic behavior must be dependent on the conformational stabilization enthalpies of all-trans and helix sequences (ΔH_1 and ΔH_2). The stabilization of the ordered sequences of these polysilanes gradually increases with the increasing size of the alkyl substituents, resulting in the appearance of the transition-type thermochromism. For example, the conformational stabilization enthalpies of poly(di-*n*-hexylsilane), which exhibits transition-type thermochromism, is 30 kJ mol^{-1}, whereas that of poly(*n*-hexylmethylsilane), which exhibits the nontransition-type thermochromism, is 0 kJ mol^{-1}. The present model calculation has suggested that the cooperation of the conformational transition is obscured if the conformational stabilization enthalpies of both all-trans and helix sequences (ΔH_1 and ΔH_2) are below 10 kJ mol^{-1}.

The present successful model suggests that transition-type thermochromism is observable only when the stabilization energies of the two ordered states between the trans and gauche sequence are large. The large conformational stabilization, which is the origin of the highly cooperative nature, must be dependent on the size of the alkyl substituents and the molecular weight (sequence length of σ-conjugation) or both. At the present stage, the highly cooperative nature may be explained by the packing of the alkyl substituents or the destabilization of a gauche (or trans) unit adjacent to all-trans (or helix) sequences due to steric repulsion between the substituents or a combination of the two.

Experimental Section

Measurements. Temperature-dependent UV spectra were recorded on a Shimadzu UV 2100 spectrometer. The temperature was varied by changing the flow rate of cold nitrogen gas and was measured with a digital thermometer placed close to the sample. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker AC-300P FT-NMR spectrometer at 300, 75.4, and 59.6 MHz, respectively. The molecular weight and molecular-weight distributions of polysilanes were measured using a JAI LC-908 gel permeation chromatograph, calibrated with polystyrene standards, with chloroform used as an eluent.

Materials. Hexane used for the spectroscopic measurements was of commercial UV spectral grade and was used without further purification. Poly(di-*n*-alkylsilane)s were prepared in the usual manner by reductive condensation of the corresponding dichlorosilane with sodium metal. A typical example is as follows.

Poly(di-*n*-hexylsilane). A solution of di-*n*-hexyldichlorosilane (8.0 g, 30 mmol) in toluene (10 mL) was added to a stirred refluxing mixture of sodium metal (1.5 g, 65 mmol) in toluene (60 mL) and diglyme (10 mL). The resulting mixture was refluxed for an additional 90 min and was then allowed to cool to room temperature. The reaction mixture was then quenched by adding a small amount of ethanol, followed by a large excess of water. After the solvent was removed, the residual mass was dissolved in benzene, and a polymer was precipitated upon pouring the solution into methanol. The treatment of dissolving–precipitating followed by freeze-drying gave poly(di-*n*-hexylsilane) as a white solid (1.9 g, 33%). The molecular weights were determined by GPC with polystyrene standards: $M_n = 2.9 \times 10^5$; $M_w/M_n = 1.9$; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.87, 1.27; ^{13}C NMR (CDCl$_3$, 75.4 MHz) δ 14.14, 15.06, 22.93, 27.62, 31.92, 34.50; ^{29}Si NMR (CDCl$_3$, 59 MHz) δ −24.98.

Poly(*n*-hexyl-*n*-propylsilane): $M_n = 3.8 \times 10^5$; $M_w/M_n = 1.9$; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.88, 0.97, 1.27; ^{13}C NMR (CDCl$_3$, 75.4 MHz) δ 14.13, 14.97, 17.55, 18.98, 20.82, 22.86, 27.48, 31.82, 34.38; ^{29}Si NMR (CDCl$_3$, 59 MHz) δ −25.08.

Poly(*n*-hexylmethylsilane): $M_n = 6.3 \times 10^4$; $M_w/M_n = 2.3$; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.22, 0.87, 1.27; ^{13}C NMR (CDCl$_3$, 75.4 MHz) δ −4.32, 14.14, 15.09, 22.75, 26.99, 31.71, 34.09; ^{29}Si NMR (CDCl$_3$, 59 MHz) δ −32.26.

Calculation of the Conformational Energies of Poly(di-*n*-alkylsilane). Calculation of the conformational energies of poly(di-*n*-hexylsilane) and poly(*n*-hexyl-*n*-propylsilane) based on the cooperative transition model and poly(*n*-hexylmethylsilane) based on the independent transition model were carried out by a personal computer with the N_{88}-Basic program. The spectral simulation of poly(di-*n*-alkylsilane) on the basis of the Monte Carlo method was also carried out by a personal computer with the N_{88}-Basic program.

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Supporting Information Available: Program for the calculation of conformational energies and spectral simulation of poly(di-*n*-alkylsilane) (14 pages). See any current masthead page for ordering and Internet access instructions.

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