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Thermochromic Behavior of Polysilanes Concerning the Dependence on the Sequence Length[1)]

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Poly(dihexylsilane) and poly(dibutylsilane) having a wide range of molecular weights were prepared by the photodegradation of the corresponding high-molecular-weight polymers. These polymers showed characteristic thermochromism. Thus, the absorption maximum observed for both polymers at around room temperature disappeared and generated a new band at longer wavelengths at low temperature. The transition temperatures (T_c) (at which the intensities of these two absorption bands become equal) of these polymers were apparently proportional to the inverse of the number-average molecular weight ($\overline{M}_n^{-1}$) until the polysilanes reach a certain value of molecular weight. Beyond that value, the transition temperature was no longer dependent on the molecular weight. The thermochromic transition temperature also depended on the size of the alkyl substituents. These results have been satisfactorily explained by a model of the thermochromism based on a cooperative transition between the ordered trans and gauche states for poly(dialkylsilane)s.

Polysilanes,[2)] a relatively new class of σ-conjugated polymers, have attracted considerable interest in recent years. Although the main chain of the polysilanes comprises saturated σ-bonds, electrons are highly delocalized along the chain, due to σ-conjugation through the silicon backbone.[3)] This conjugation has been considered to be the origin of the intense absorption of polysilanes in the near-ultraviolet region, which is strongly coupled with the polymer σ backbone.

In addition, poly(dialkylsilane) exhibits a variety of quite unique thermochromic behaviors, which depend upon the nature of the alkyl substituents.[4)] As the temperature of a solution of polysilanes decreases, bathchromic shifts of the principal σ–σ^* absorption bands in the ultraviolet region are observed. This change may occur gradually, along with a continuous red shift of the ultraviolet absorption band, or abruptly, as the original absorption band decreases in intensity, along with the appearance of a new band at longer wavelengths. Polysilane of a well-studied example of the latter type is poly(dihexylsilane), which undergoes a transition at ca. −30 °C in hexane, with a UV absorption shift from $\lambda_{\max}$ 315 to 354 nm.

We recently presented a successful model of thermochromism based on a cooperative transition between the ordered trans and gauche states for poly(dialkylsilane)s.[5)] In this model, the enthalpy of stabilization of both the trans and gauche sequences were calculated to be ca. 7 $\mathrm{kcal\,mol^{-1}}$ for poly(dihexylsilane). The very large value of stabilization energies of the trans and gauche sequence must be dependent on the size of the alkyl substituents and/or on the sequence length of σ-conjugation. It is therefore of interest to investigate the dependence of the thermochromic behavior of poly(dialkylsilane) in solution on the sequence length. It is also important to uncover the relationship between the conformation and sequence length of polysilanes in general.[6)] Herein, we report that the unique thermochromism of poly(dialkylsilane) depends strongly on the sequence length of the polymer.

Experimental

Materials. High-molecular-weight poly(dihexylsilane) and poly(dibutylsilane) were prepared in the usual manner by reductive condensation of the corresponding dichlorosilane with sodium metal.[7)] A typical example of synthesis of the high-molecular-weight polysilane is as follows. A solution of dihexyldichlorosilane (7.5 g, 28 mmol) in toluene (10 ml) was added to a stirred refluxing mixture of sodium metal (1.5 g, 64 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 amount of water. After removing the solvent the residual mass was dissolved in benzene, and a polymer was precipitated upon pouring the solution into methanol. The treatment of dissolving-precipitation followed by freeze-drying gave poly(dihexylsilane) as a white solid (1.7 g, 30%). The molecular weights were determined by GPC with polystyrene standard; $\overline{M}_n=7.6\times10^4$, $\overline{M}_w/\overline{M}_n=2.1$. Poly(dibutylsilane) was prepared in similar manner to that described above (32%, $\overline{M}_n=2.7\times10^5$, $\overline{M}_w/\overline{M}_n=3.3$).

Photodegradation. High-molecular-weight polysilanes were then degradated photochemically as follows.[8)] A solution of poly(dihexylsilane) (0.10 g) in hexane (10 ml) bubbled with argon gas was irradiated for several minutes with a 500 W high-pressure mercury lamp equipped with selected cutoff filters ($\lambda \geq 320$ nm). After evaporating the solvent, the resulting relatively low molecular-weight polysilanes were characterized by NMR and GPC (polystyrene standard). The ^{1}H NMR spectra of the lowest molecular weight poly(dihexylsilane) ($\overline{M}_n=2.0\times10^3$) showed a broad signal at 3.8 ppm, which was assigned to Si–*H* of the polymer ends. The molecular weight calculated from the ^{1}H NMR was 1.3×10^3.

Measurements. Hexane used for the spectroscopic measurements was of commercial UV spectral grade, and was used without further purification. Temperature-dependent UV spectra were recorded on a Shimadzu UV2100 spectrometer. The temperature was varied by changing the flow rate of cold nitrogen gas, and was measured with a digital thermometer placed near 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.

Results and Discussion

Preparation of Samples by Photodegradation of Poly(dihexylsilane). The requisite polysilanes of relatively low molecular weight were prepared by the photodegradation of poly(dialkylsilane) of high molecular weight with long-wavelength ($\lambda \geq 320$ nm) light in hexane.[9] An example of the degradation of poly(dihexylsilane) in hexane is shown in Fig. 1. The observation of a progressive blue shift in the absorption maximum suggested that the polymer was being continuously degradated upon exposure by the chain scission process.[10] Accordingly the number-average molecular weight of these polysilanes decreased progressively by photodegradation as followed by GPC. Photodegradation of poly(dibutylsilane) was carried out in a similar manner.

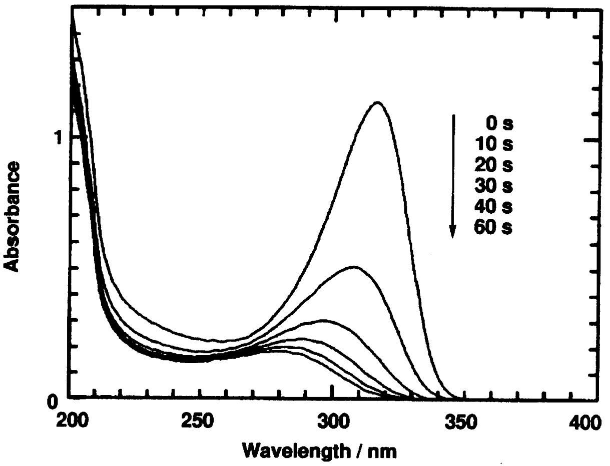

Fig. 1. UV spectral change of poly(dihexylsilane) in hexane upon irradiation at $\lambda \geq 320$ nm.

Thermochromic Behavior of Poly(dialkylsilane) of Various Molecular Weight in Hexane. The absorption spectra of the polysilanes with a wide range of molecular weights from 2.7×10^5 to 2.0×10^3 gradually changed depending on the molecular weight. The dependence of the absorption maxima of these polysilanes on the molecular weight at 25 °C is shown graphically in Fig. 2. The $\lambda_{\max}$ (25 °C) initially increased with increasing molecular weight, approaching a limiting value of a number-average molecular weight of around 1.0×10^4, similar to those observed previously.[6b)]

Next, the thermochromic behaviors of these poly(dialkylsilane) with a wide range of molecular weights were measured in hexane. The thermochromic behavior of poly(dihexylsilane) with a molecular weight of $\overline{M}_n=2.9\times10^3$, for example, showed an abrupt bathochromic shift from 290 to 315 nm in the temperature range from −50 to −75 °C, as shown in Fig. 3. The absorption at 290 and 315 nm correspond to the helical-gauche and all-trans forms, respectively.[4,11)] The relative absorbance of bands corresponding to the helical-gauche

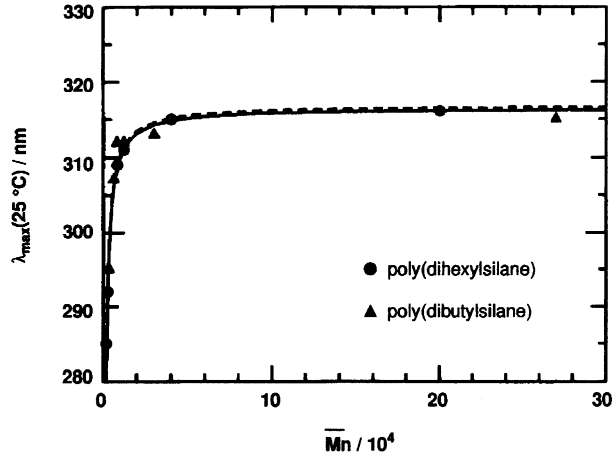

Fig. 2. Absorption wavelength maxima at 25 °C as a function of the molecular weight: (●) poly(dihexylsilane); (▲) poly(dibutylsilane).

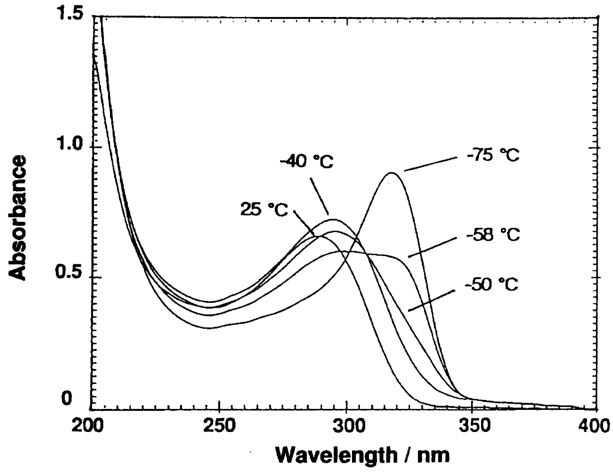

Fig. 3. Thermochromic behavior of poly(dihexylsilane) of low molecular weight ($\overline{M}_n=2.9\times10^3$).

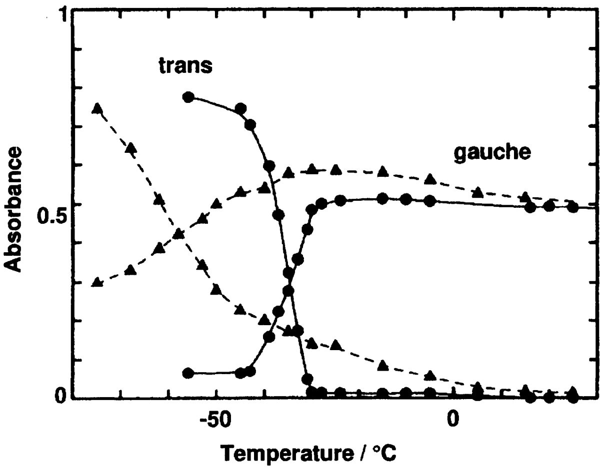

Fig. 4. Absorbance of *helical*-gauche and *all*-trans sequences in hexane plotted as a function of temperature for high molecular weight (●, $\overline{M}_n=2.0\times10^5$) and low molecular weight (▲, $\overline{M}_n=2.9\times10^3$) poly(dihexylsilane).

and the all-trans are plotted in Fig. 4 as a function of the temperature for the low-molecular-weight poly(dihexylsilane) together with that of high-molecular-weight poly(dihexylsilane) ($\overline{M}_n$=2.0×10^5). As shown in Fig. 4, the intensities of the all-trans increase with decreasing temperature, while those of the helical-gauche decrease. The transition of the high-molecular-weight polysilane occurred within a very narrow range of temperature, while the transition of the low-molecular-weight polysilane occurred at a lower and wider temperature range. The transition temperature (T_c), at which the intensities of the two absorption bands become equal, was −58 and −34 °C for the low and high molecular weight polymers, respectively.

In this way, the transition temperatures (T_c) of poly(dihexylsilane) and poly(dibutylsilane) with various ranges of molecular weight were estimated, and are shown in Tables 1 and 2.

The dependence of the thermochromic transition temperatures on the molecular weights for poly(dihexylsilane) and poly(dibutylsilane) is shown in Fig. 5, both with $\overline{M}_n$ and $\overline{M}_n^{-1}$.

Table 1. Molecular Weight Dependence of the Transition Temperature and Absorption Wavelength Maxima at 25 °C for Poly(dihexylsilane)

$\overline{M}_n/10^4$	λ_{max} (25 °C)/nm	T_c/°C
20	316	−34
4.0	315	−36
1.2	311	−46
0.08	309	−53
0.29	292	−58
0.20	285	−79

Table 2. Molecular Weight Dependence of the Transition Temperature and Absorption Wavelength Maxima at 25 °C for Poly(dibutylsilane)

$\overline{M}_n/10^4$	λ_{max} (25 °C)/nm	T_c/°C
27	315	−38
3.0	313	−48
1.2	312	−52
0.80	312	−53
0.62	307	−59
0.33	295	−80

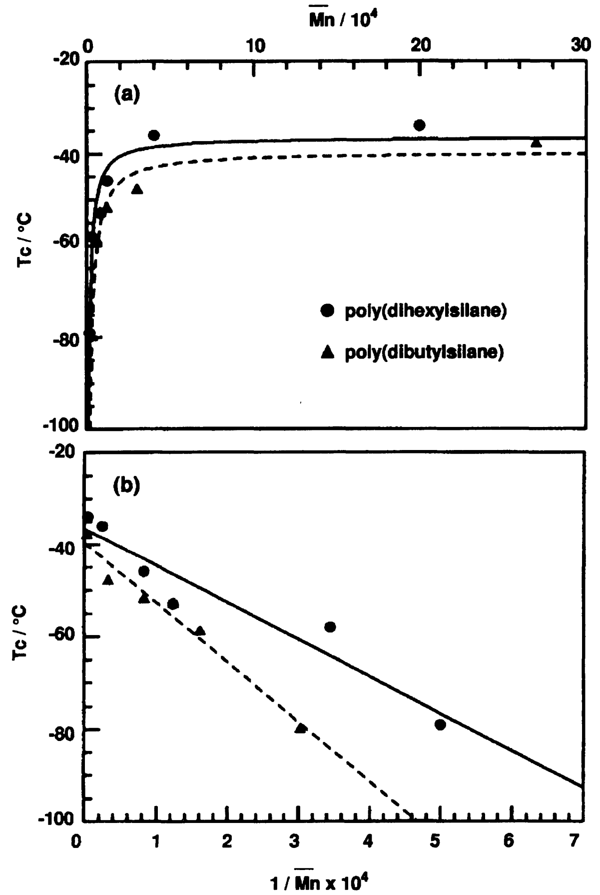

Fig. 5. Molecular weight dependence of the transition temperature of the thermochromism for poly(dihexylsilane) and poly(dibutylsilane): (a) against $\overline{M}_n$ and (b) $\overline{M}_n^{-1}$.

As shown in Fig. 5b, the transition temperature (T_c) of poly(dihexylsilane) and poly(dibutylsilane) are apparently proportional to the inverse of the number-average molecular weight ($\overline{M}_n^{-1}$) in the low molecular weight region. Therefore, the molecular weight ($\overline{M}_n$) dependence on the transition temperature (T_c) of poly(dialkylsilane) can be expressed in the following form in the region:[12)]

$$T_c = T_\infty - k_0/\overline{M}_n, \tag{1}$$

where T_c is a transition temperature for a polymer of a number-average molecular weight of $\overline{M}_n$, T_∞ is the same property evaluated at infinite molecular weight, and k_0 is a coefficient (Table 3).

The linear relationship between the inverse of the

Table 3. Parameters of the Molecular Weight Dependence of the Transition Temperature of Poly(dihexylsilane) and Poly(dibutylsilane)

	T_∞/°C	k_0
Poly(dihexylsilane)	−36	8.0×10^4
Poly(dibutylsilane)	−39	1.2×10^5

molecular weight ($\overline{M}_n^{-1}$) and the transition temperature (T_c) indicates that the transition temperature is dependent on the molecular weight until the polysilane reaches to a certain value of molecular weight. Beyond that value, the transition temperature is no longer dependent on the molecular weight. This kind of leveling-off has been observed for the UV spectra of polysilanes as can be seen in Fig. 1, as well as for other phenomena of polymers.[13)]

The cooperative transition model for thermochromism of poly(dialkylsilane) suggested that transition type thermochromism is observable only when the stabilization energies of the two ordered states between the trans and gauche sequence are large. Therefore, even though the dependence of the thermochromism on the molecular weight is limited to relatively low molecular weight polysilanes, the stabilization of the sequence length of these polysilanes must play a significant role in the appearance of thermochromism of the transition type for poly(dialkylsilane). The inverse of the number-average molecular weight is associated with the number of end groups of the polymer. Since the stabilization is regarded as being the nearest neighbor interaction of the trans and gauche sequences, the end group of the polymer, with a relatively large degree of freedom, must exert a strong influence on the stabilization of the sequence length. As a result, the transition temperatures of these polysilanes are dependent on the sequence length.

There is another important fact which must be pointed out concerning the dependence of the thermochromic transition temperature on the sequence length. The values of the proportionality constant (k_0) are related to the size of alkyl substituents; namely, the constant of poly(dihexylsilane) (k_0) is two-fold smaller than that of poly(dibutylsilane), as shown in Table 3. At this moment, since we only have two examples, it may be premature to deduce any definite conclusions, though it is likely to be suggested that the stabilization caused by the alkyl substituent of these polymers must increase along with increasing size of the alkyl substituents. As a result, a larger stabilization of the sequences was observed for poly(dihexylsilane) with a lower molecular weight than that for poly(dibutylsilane).

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