# Remarkable Temperature Dependence of Two-Photon Absorption Spectrum of Poly(dihexylsilylene) in Solution

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The nonresonant two-photon absorption spectrum of poly(dihexylsilylene) (**1**) in 3-methylpentane solution showed an abrupt thermochromism with a similar transition temperature to the one-photon absorption spectrum of **1**. The parallel temperature dependence between the one-photon and two-photon absorption spectra suggests that the two-photon excited state involves an important contribution of the σ–σ* excited electronic configurations.

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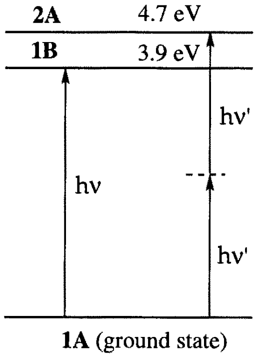
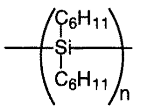
Much attention has been focused on the distinct low-lying two-photon excited states of linear polysilanes with effective σ-conjugation,[1] which resembles π-conjugation in linear polyenes. As shown in Figure 1, the two-photon allowed excited state of poly(dihexylsilylene) (PDHS) has been found at 0.8 eV above the one-photon allowed lowest excited state in hydrocarbon glass and in thin films,[2] in contrast to the two-photon excited states of linear polyenes,[3] which are about 0.5 eV below the one-photon allowed lowest excited states. The two-photon allowed excited state of PDHS should have the same symmetry to the ground state (A symmetry) within the applicable point group, because of the two photon polarization parameter $I_c/I_l$ of 0.65 ± 0.3,[2] where $I_c/I_l$ is the ratio of the two-photon intensity for the circularly and linearly polarized radiation. Although a number of experimental and theoretical studies have been reported for the nature of the two-photon allowed excited state of polysilanes,[2,4–6] no secure assignment of the 2A excited state has been given until now.





PDHS

**Figure 1.** Relative energy levels of one-photon and two-photon excited states of poly(dihexylsilylene) (PDHS).

During the course of our study of the nonresonant two-photon photochemistry of polysilanes,[7] we have found remarkable temperature dependence of the two-photon absorption spectrum of PDHS with the same transition temperature to the one-photon thermochromism. The present study constitutes the first observation of the temperature dependence of the two-photon absorption spectrum of PDHS in solution, while the two-photon absorption spectra in solution and in thin films were investigated at several limited temperatures.[2,4,5]

Two-photon absorption spectrum of PDHS (**1**, $M_n$ = 366000, $M_n/M_w$ = 1.23, monomodal)[8] in 3-methylpentane solution was measured at various temperatures (170–290 K) by the two-photon fluorescence method.[9,10] As shown in Figure 2, a broad absorption band of **1** in the solution showed a small red-shift with lowering temperatures from 290 K to 250 K; $\lambda_{max}$ = 260 nm at 290 K but 270 nm at 250 K. When the temperature reached 240 K, the original broad band was replaced abruptly by a new rather sharp band at 287 nm. With lowering temperatures from 240 K to 170 K, the band became much sharper but the maximum did not shift. The two-photon thermochromic behavior is quite parallel to the well-known thermochromism of the one-photon absorption band of **1**, which is known to show a continuous red-shift from 314 nm at room temperature to 320

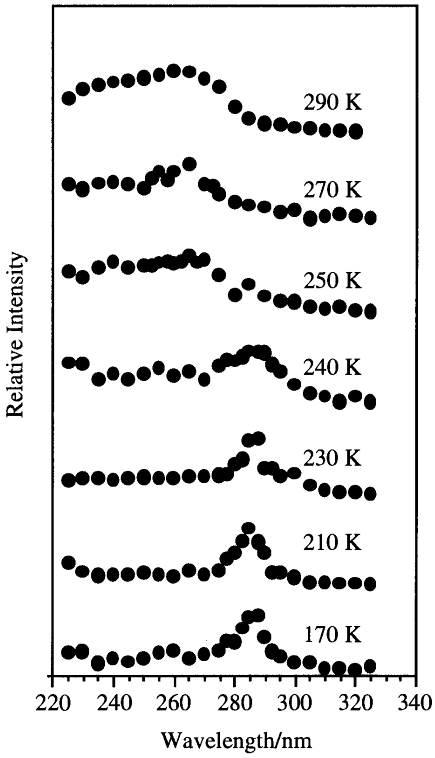


**Figure 2.** Temperature dependent two-photon absorption spectra of **1** in 3-methylpentane at various temperatures.

nm at 250 K followed by the abrupt formation of a new narrow and intense band at 353 nm at lower temperatures than 250 K.[11]

The transition temperature of the two-photon absorption of **1** is very close to that of the one-photon band. The energy difference between the 2A and 1B excited states ($\Delta E_{2A-1B}$) is almost independent of temperature; the $\Delta E_{2A-1B}$ value is estimated to be 0.83 and 0.85 eV at 290 and 240 K, respectively.

The lowest one-photon (1B) state of a linear polysilane is well documented to be the lowest $\sigma$–$\sigma^*$ excited state formed by the one-photon excitation from the $\sigma_{HOMO}$ to the $\sigma^*_{LUMO}$. Since the HOMO–LUMO gap is strongly dependent on the conformation of the polysilane main chain, the origin of the thermochromism of the one-photon spectra of linear polysilanes like PDHS is usually ascribed to the conformational transition of the silicon backbone at low temperatures from a random coil to a pseudo-trans rod.[11,12] The parallel temperature dependence between 1B and 2A absorptions of PDHS may indicate that the two absorptions engage with the random-coil to trans-rod transition of the main chain, and hence, that the two-photon absorption involves an important contribution of the $\sigma$–$\sigma^*$ transition.

The two-photon excited states of PDHS have been rationalized on the basis of a qualitative MO theory[5,6] and on the exciton theory.[2,4] Typically, Soos and Hayden[5] have extended the Sandorfy C model for $\sigma$ conjugation in linear polysilanes,[13] where the molecular orbitals of the Si chain are represented by a linear combination of the $sp^3$ orbitals at silicon, to include electron repulsion (the Pariser–Parr–Pople type calculations), to explain the relative energy levels of the lowest one-photon (1B) and two-photon excited (2A) states.[5] Whereas the Sandorfy C method is topologically similar to the Hückel method for $\pi$ conjugation in a polyene, the important difference between the $\sigma$ and $\pi$ conjugation is in the significant alternation in the $\sigma$ conjugation; in polysilane, the vicinal resonance integral $\beta_{vic}$ has much larger negative value than the geminal resonance integral $\beta_{gem}$, while the alternation ($\beta/\beta'$) is small in polyene. The reason that the 1B state is lower in energy than the 2A state in PDHS was ascribed thus to the significant alternation in the $\sigma$ conjugation.[14] On the other hand, Tachibana et al.[4] have reported electroabsorption spectrum of a thin film of PDHS and the results were explained with the one-dimentional molecular crystal model;[4e] the 1B and 2A states were assigned to the first and second states associated with the same $\sigma$–$\sigma^*$ interband transitions on the chain.

The above two representative models seem to be compatible basically with the observed parallel temperature dependence of the one-photon and two-photon absorption bands of PDHS in solution, while the conformational dependence of the electronic nature of PDHS is not taken into account explicitly in these models. Further detailed theoretical studies are desirable to elucidate the electronic excited states of these interesting $\sigma$-conjugated polymers.

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