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Supplementary Material Available: Tables of conditions and parameters for the X-ray diffraction studies, positional and thermal parameters, and observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

Organosilane High Polymers: Thermochromic Behavior in Solution

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Summary: Aliphatically substituted polydiorganosilylenes display reversible thermochromic behavior in solution with a bathochromic shift occurring with decreasing temperature. Solutions of polymers (RMeSi)_n, R = *n*-propyl and *n*-hexyl, and poly(di-*n*-propylsilylene) show gradual bathochromic shifts of 16–25 nm from 92 to –67 °C. In polymers containing long di-*n*-alkyl substituents (*n*-alkyl = *n*-butyl, *n*-pentyl, and *n*-hexyl) the principal absorption band disappears as the temperature is lowered and a new band appears at 354 nm, giving a total red shift of up to 44 nm. The temperature dependence of the UV absorption maxima is thought to be due to conformational changes occurring along the polymer backbone with temperature.

Organopolysilenes, because of their remarkable long wavelength absorption spectra,¹ offer a unique opportunity² to observe the dependence of electronic transition energy on backbone conformation. These polymers display an intense UV absorption band, described as a delocalized $\sigma \rightarrow \sigma^*$ or a $\sigma \rightarrow 3d$ transition, in the mid-UV region. The position of the band (λ_{\max}) and its absorptivity per Si–Si bond ($\epsilon_{\text{Si-Si}}$) increase regularly with increasing chain length, finally becoming constant for very long chains. The absorption maxima at room temperature ($\lambda_{\max\text{RT}}$) exhibit a red shift with increasing size of the alkyl substituent with $\lambda_{\max\text{RT}}$ in the range from 305 to 326 nm. The variation of $\lambda_{\max\text{RT}}$ with substituent bulk has been attributed to conformational changes about the polysilane skeletal framework¹ induced by interactions between adjacent Si-bound

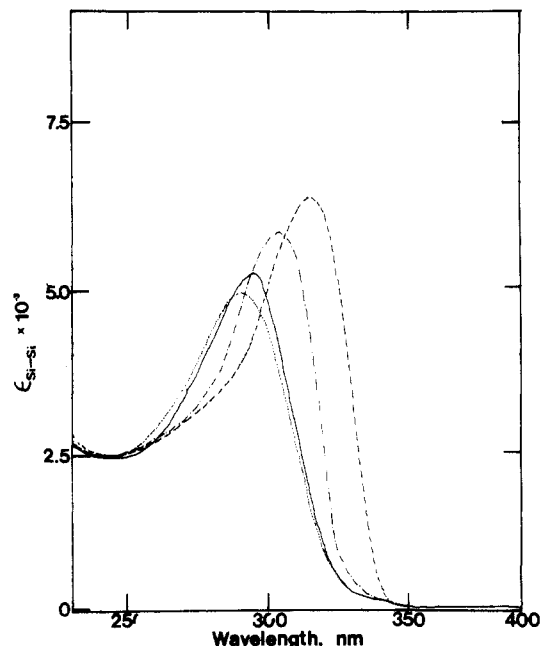


Figure 1. UV spectrum of a 0.0035% solution of (*n*-HexMeSi)_n in isooctane: (···), 92 °C; (—), 24 °C; (---), –17 °C; (-·-·), –67 °C.

substituents, which alter the overlap between geminal or 1,3 Si–Si σ orbitals and change the orbital energies.^{3,4}

Recently a temperature-dependent change of the UV spectrum has been observed for films of poly(di-*n*-hexylsilylene)^{5,6} and attributed to crystallization of the side chains in the solid.⁵ We have now examined the UV spectra of solutions of several polysilylenes as a function of temperature and find that striking and unprecedented thermochromic changes in the UV absorption also occur in solution.

Three distinct types of thermochromic behavior have been observed for poly(dialkylsilylenes). The first is exemplified by poly(*n*-propylmethylsilylene), 1, poly(*n*-hexylmethylsilylene), 2, and poly(di-*n*-propylsilylene), 3 [$\lambda_{\max\text{RT}}$ 305 (1), 306 (2), and 310 nm (3)].⁷ In these polymers, λ_{\max} undergoes a continuous bathochromic shift of 25 nm for 1, 16 nm for 2, and 22 nm for 3 (Figure 1) on cooling from 92 to –67 °C. We believe this thermochromism is probably due to a continuously increasing relative population of trans conformation in the polymer backbone with cooling.^{8,9}

(3) It has been shown that the energies of the delocalized $\sigma_{\text{Si-Si}}$ HOMO in tetrasilane and pentasilane vary with molecular conformation: Bock, H.; Ensslin, W.; Feher, F.; Freund, R. *J. Am. Chem. Soc.* 1976, 98, 668.

(4) Full relaxation, empirical force field calculations for poly(dimethylsilylene) reveal that this polymer adopts the gauche conformation in the ground state. However, if the VDW radii of the methyl groups are increased to simulate increasing substituent bulk, the trans conformation becomes increasingly preferred. Damewood, J. R.; West, R., unpublished results.

(5) Miller, R. D.; Hofer, D.; Rabolt, J.; Fickes, G. N., submitted for publication in *J. Am. Chem. Soc.*

(6) Harrah, L. A.; Zeigler, J. M. *J. Polym. Sci., Polym. Lett. Ed.*, in press.

(7) All polymers used (except 1, $\bar{M}_w = 3.0 \times 10^4$, and 6, $\bar{M}_w = 4.0 \times 10^4$) are of high molecular weight, with \bar{M}_w in excess of 5.0×10^6 . Ultraviolet spectra were taken in isooctane for 1–3, hexane for 4–1, and methylcyclohexane for 7.

(8) Conformations of polymers in solution are frequently temperature dependent; see: Elias, H.-G. In "Macromolecules"; Plenum Press: New York, 1976; Chapter 4.

(9) A qualitative LCAO model predicts that the $\sigma_{\text{Si-Si}}$ HOMO–LUMO energy separation will be smaller in the trans conformation than the gauche. The UV absorption would therefore be expected to red shift with increasing trans population in the polymer backbone. These predictions have been confirmed by MNDO calculations on tetrasilabutane and by molecular mechanics calculations on 6. Damewood, J. R., unpublished results.

(1) (a) Trefonas, P. III; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* 1983, 21, 823. (b) West, R. In "Ultrastructure Processing of Ceramics, Glass and Composites"; Hench, L., Ulrich D. R., eds. Wiley: New York, 1984; Chapter 19. (c) Miller R. D.; Hofer, D.; Willson, C. G.; West, R.; Trefonas, P. In "Materials for Microlithography"; Thompson, L., Willson, C. G., Frechet, J. M. J., Eds.; American Chemical Society: Washington, D.C., 1984; ACS Symp. Ser. No. 266, p 293.

(2) Patel, G. N.; Chance, R. R.; Witt, J. D. *J. Chem. Phys.* 1979, 70, 4387.

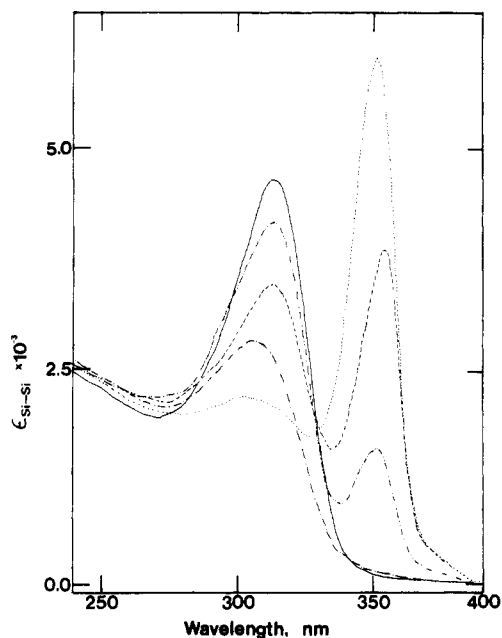


Figure 2. UV spectrum of a 0.0055% solution of $(n\text{-Bu}_2\text{Si})_n$ in hexane: (---), 72 °C; (—), 18.5 °C; (·····), -18.5 °C; (-·-·-), -38 °C; (---), -61 °C.

The second group of polysilylenes ($n\text{-alkyl}_2\text{Si}$) $_n$ [$n\text{-alkyl} = n\text{-butyl}$ (4), $n\text{-pentyl}$ (5), and $n\text{-hexyl}$ (6); λ_{maxRT} 314 (4), 315 (5), and 316 nm (6)] show different thermochromic behavior. Dilute solutions of 4 display a continuous red shift in the absorption maxima of 307–314 nm as the solution is cooled from +72 to -10 °C. Then a new intense band at 354 nm gradually develops as the temperature is lowered from -10 to -61 °C (Figure 2), with the midpoint of the equilibrium from the 314-nm band to the 354-nm band occurring at -25 °C. Solutions of 6 show a similar continuous red shift from 311 nm at 56 °C to 320 nm at -24 °C followed by the sudden formation at -24 °C (over a $\sim 2^\circ$ range) of a new extremely narrow and intense band at 353 nm (Figure 3). Solutions of 5 display UV behavior intermediate to that of 4 and 6, with the appearance of the 354-nm band occurring over a shorter range than for 4; the midpoint for this equilibrium is ~ -2 °C. Further cooling of solutions of all three polymers produces no change in the absorption maximum, only a narrowing of the band at ca. 354 nm. The thermochromic behavior of 4–6 is reversible upon warming and is independent of concentration over a tenfold change from 0.005% to 0.0005% by weight.

The thermochromism of solutions of 4–6 somewhat resembles that of solid films of 6, in which a new UV band at 370 nm appears upon cooling.^{5,6} In both cases the new absorption may reflect ordering of the polymer into a more extended conformation, but the mechanics in solution must be different from those in solid films. One possible explanation is that microcrystals form below the transition temperature; upon long standing below this temperature precipitation of the polymer does take place. Another possibility is that interaction between the $n\text{-alkyl}$ side chains on different parts of the polymer backbone could lead to folding into a "hairpin" configuration, in which the

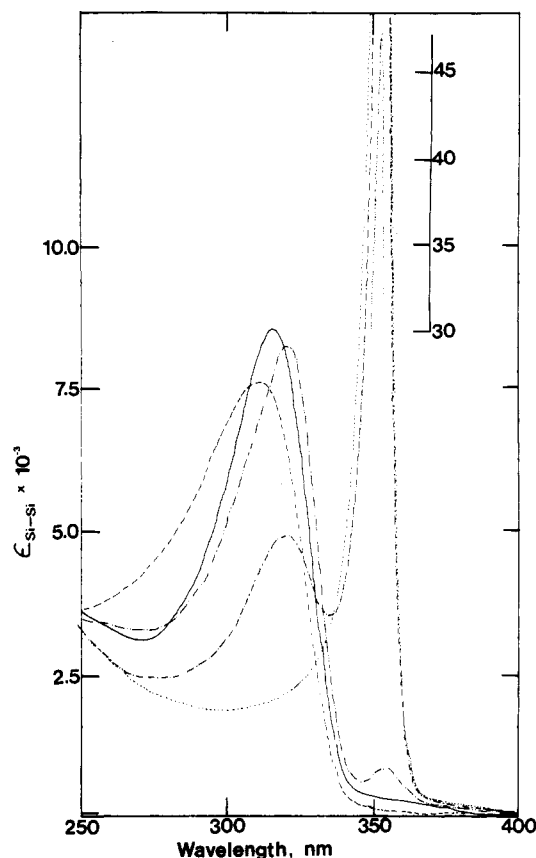


Figure 3. UV spectrum of a 0.0045% solution of $(n\text{-Hex}_2\text{Si})_n$ in hexane (---), 56 °C; (—), 24 °C; (·····), -23.5 °C; (-·-·-), -24.2 °C; (---), -54.5 °C.

trans conformation at the silicon atoms in the straight portions of the chain would be enforced; still a third explanation is that the polymers undergo a rod-to-coil transformation as prepared by other workers for 6.¹⁰ This change evidently takes place over a wide temperature range for 4 but quite abruptly for 6, in which the larger $n\text{-hexyl}$ groups could interact more strongly.

A third type of behavior is shown by poly(cyclohexylmethylsilylene), 7, which shows little temperature dependence of the UV absorption spectra. Only a slight bathochromic shift from 321 to 328 nm occurs upon cooling from 90 to -64 °C. The λ_{max} for this polymer is substantially red-shifted relative to 1–6 at high temperatures, perhaps reflecting the fact that steric interactions between substituents have already caused substantial alignment of the polymer backbone.

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