Macromolecules **2001,** *34,* 6003−6004 **6003**

Thermochromism of Poly(di-*n*-hexylsilane) in Solution Revisited

Sergey S. Bukalov and Larissa A. Leites

Scientific and Technical Center on Raman Spectroscopy, Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow 117813, Russia

Robert West*

Organosilicon Research Center, Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706

Received January 30, 2001; Revised Manuscript Received May 7, 2001

ABSTRACT: Solutions of poly(di-*n*-hexylsilane) in hexane, after aging for 5 days, exhibit on cooling two long-wavelength absorption bands at 357 and 368 nm, in addition to the normal high-temperature band at 320 nm. These UV absorptions probably represent different conformations of the polymer chain and so provide evidence for the simultaneous presence in solution of three different conformational forms. This is the first time such an observation has been made for a polysilanes and perhaps for any polymer.

The UV thermochromism of polysilane polymers in solution, first reported in 1986,[1,2] has been the subject of numerous experimental and theoretical studies.[2−10] For many polysilanes, as the temperature is decreased, the prominent $\sigma-\sigma^*$ absorption band near 320 nm is replaced by one at longer wavelength. These different bands are believed to represent different polymer chain conformations, which exist in equilibrium in polysilane solutions.

This thermochromism was first observed for poly(di-*n*-hexylsilylene), PDHS, which has become probably the best studied of all polysilanes. According to previous reports,[1−4] solutions of PDHS at room temperature exhibit a broad absorption near 320 nm (band I). As the temperature is decreased to −50 °C, this band decreases in intensity and a new absorption (band II) grows in at ~357 nm, indicating straightening of the polysilane chain leading to greater σ-conjugation. The thermochromism is reversible upon warming.

We now find that under some circumstances PDHS may exhibit an absorption at 368 nm (band III) in addition to those at 320 and 357 nm. The 368 nm absorption band probably represents an even more extended form of the polymer. This is the first time that *three* different conformations of a polysilane, and perhaps of any polymer, have been observed simultaneously in solution.[11]

Experimental Section

PDHS was prepared by the usual sodium condensation of di-*n*-hexyldichlorosilane[3] and purified by reprecipitation from toluene with 2-propanol. The purified polymer was monomodal with M_w 1 708 000 and polydispersity 2.3 (GPC, polystyrene standards). A solution of the polymer, between 10^{-5} and 10^{-6} mol (Si unit) L^{-1} in hexane, was placed in a specially constructed, hermetically sealed, temperature-controlled metal cell with quartz windows and optical path = 50 mm. The temperature was controlled with a Pt resist (R = 100 ohm), placed directly into the solution. The temperature was maintained with an accuracy of ±1 °C in the interval from +20 to −60 °C. UV spectra were determined with a computerized Carl Zeiss M40 spectrophotometer.

Results and Discussion

Figure 1 shows the evolution of the electronic spectrum of a freshly prepared solution of PDHS on fast cooling. Between +20 and −40 °C, band I shifted gradually to longer wavelength, from 317.5 to 322 nm (Figure 1a, Table 1). Upon further cooling from −40 to −55 °C, band I disappeared and band II grew in (Figure 1b). The change was rapidly reversible upon warming. This is the classical “type 3” behavior for polysilanes in solution.[3,4] Band II is quite narrow, with half-width $\Delta\nu_{1/2}$ = 650 cm^{-1}.

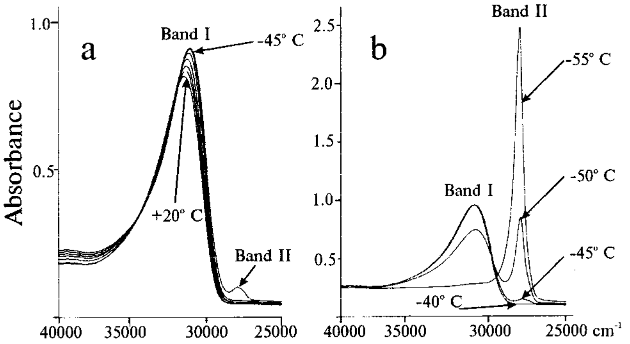

Figure 1. Temperature evolution of the UV spectrum of PDHS upon rapid cooling of the fresh solution. Cooling from +20 to −45 °C (a) and from −40 to −55 °C (b).

Analogous experiments with the same solution carried out during the next 4 days gave the same results. However, on the fifth day, while carrying out rapid cooling in the identical manner, it was noticed that band II had become broader, $\Delta\nu_{1/2}$ = 1000 cm^{-1}. When the solution was immediately reheated, band II once again disappeared, but as shown in Figure 2, at 0 °C a small, third absorption was observed at 368 nm (band III). On further heating to room temperature, band III became less intense but did not disappear completely; this happened only after keeping the solution at room temperature overnight.

When the aged PDHS solution was cooled under quasi-equilibrium conditions (that is, very slowly, in a stepwise manner, each temperature being maintained not less than half an hour until the spectral pattern stabilized), band III appeared first in the interval from −10 to −20 °C, prior to formation of band II. The latter became noticeable only at −45 °C and then grew in and became dominant with further cooing. Detailed behavior of bands II and III upon slow cooling of the solution from

10.1021/ma0101714 CCC: $20.00

Table 1. Temperature Dependence of λ_{max} of the UV Bands Observed for $[^nHex_2Si]_n$ Solution in Hexane

temp, °C	+20	−5	−15	−25	−35	−40	−45	−50	−55
band I, nm	317.5	318.8	319.4	320.1	320.7	322	322.6	323.5	
band II, nm							358	357	356
band III, nm				367.8		366		364.8	

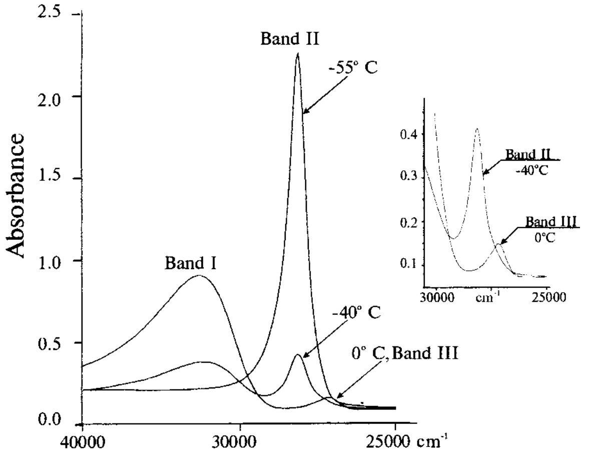

Figure 2. First detection of band III during heating of the aged solution from −55 to 0 °C.

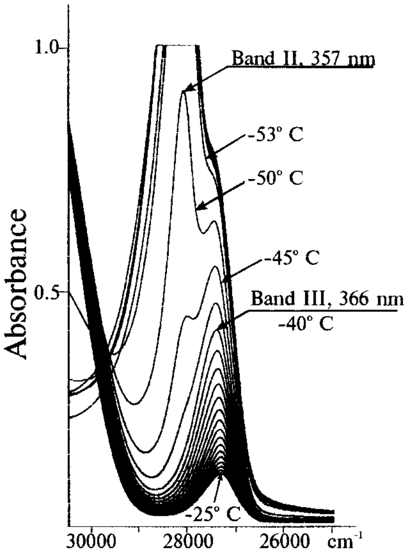

Figure 3. Temperature evolution of the UV spectrum of PDHS in solution upon slow cooling from −25 to −60 °C. Only the region 330−400 nm is presented, where bands II and III of more ordered forms are situated.

−25 to −60° C is illustrated in Figure 3. Band III grew in slowly as the temperature was decreased, its half-width being ca. 750 cm^{-1}. At about −45 °C band II began to grow in, much more rapidly. Below −50 °C band III correspondingly revealed itself only as a shoulder on the more prominent band II absorption. As shown in Table 1, bands II and III both blue shift slightly upon cooling, as is typical for the UV absorptions for ordered polysilane macromolecules.[12]

When the solution of Figure 3 was warmed slowly, band II disappeared promptly, but band III persisted even up to room temperature. The latter band disappeared only over about 16 h at 20° C.

These observations may be interpreted as follows.

1. Band I, at ca. 320 nm, corresponds to a disordered form of the polymer, since it is very broad ($\Delta\nu_{1/2} = 3000$ cm^{-1}) and red-shifts upon cooling, consistent with gradual straightening of the polysilane chain.

2. The band I and band II forms of the polymer are in rapid equilibrium.

3. Band II must represent an ordered form of the polysilane chain but cannot be all-anti (trans) as suggested in the earlier literature. A possible arrangement is a transoid helix, with Si−Si−Si−Si torsional angles near 165°.[3,13]

4. Band III also represents an ordered arrangement of the polysilane chain, with greater torsional angles, perhaps anti (trans) or near anti. The slow, kinetically limited disappearance of this form upon warming, and the fact that it appears only in aged solutions, suggests that it may be due to the gradual reversible aggregation of polymer molecules. Aggregation of PDHS in solution has been observed previously in light-scattering studies.[7,8]

Our results show that PDHS can exist in three different conformational forms in solution, not two as previously reported. Two of the forms are in rapid equilibrium, but the third equilibrates only slowly. In the future fluorescence emission and excitation spectra for these forms will be investigated, to examine the possibility of excitonic interactions as reported earlier for $Si_{16}(CH_3)_{34}$,[14] and other polysilanes will be studied to see whether they also exhibit such multiple conformations in solution.

Acknowledgment. This work was supported by the National Science Foundation, the Organosilicon Research Center, and the Russian Foundation for Basic Research, Grant 01-03-33057.

References and Notes

(1) Harrah, L. H.; Zeigler, J. M. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 209.
(2) Trefonas III, P.; Damewood, J. R.; West, R.; Miller, R. D. *Organometallics* **1985**, *4*, 1318.
(3) For a summary see: Michl, J.; West, R. Electronic Structure and Spectroscopy of Polysilanes. In *Silicon-Based Polymers: The Science and Technology of their Synthesis and Applications;* Chojnowski, J., Jones, R. G., Ando, W., Eds.; Kluwer: Dordrecht, The Netherlands, 2000; pp 499−529.
(4) Sanji, T.; Sakamoto, K.; Sakurai, H.; Ono, K. *Macromolecules* **1999**, *32*, 3788.
(5) Schweitzer, K. S. *J. Chem. Phys.* **1986**, *85*, 1156, 1176.
(6) Klingensmith, K. A.; Downing, J. W.; Miller, R. D.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 7438.
(7) Cotts, P. M.; Miller, R. D.; Trefonas III, P.; West, R.; Fickes, G. *Macromolecules* **1987,** *20*, 1046.
(8) Shukla, P.; Cotts, P. M.; Miller, R. D.; Russell, T. P.; Smith, B. A.; Waalraff, G. M.; Baier, M.; Thyagarajan, P. *Macromolecules* **1991**, *24*, 5606.
(9) Miller, R. D.; Waalraaf, G. M.; Baier, M.; Cotts, P. M.; Shukla, P.; Russell, T. P.; De Schryver, F. C.; Declerq, D. *J. Inorg. Organomet. Polym.* **1991**, *1*, 505.
(10) Oka, K.; Fujiue, N.; Nakanishi, S.; Takata, T.; West, R.; Dohmaru, T. *J. Organomet. Chem.* **2000**, *611*, 45.
(11) Multiple conformations in the solid state are common, and many examples are known among the polysilanes; see ref 3.
(12) Bukalov, S. S.; Leites, L. A.; West, R., unpublished studies.
(13) Michl, J.; West, R. *Acc. Chem. Res.* **2000**, *33*, 821.
(14) Sun, Y.-P.; Hamada, Y.; Huang, L.-M.; Maxka, J.; Hsiao, J.-S.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 6301.

MA0101714