Side-Chain Effect on the Nature of Thermochromism of Polysilanes

Chien-Hua Yuan and Robert West*

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received May 4, 1993

Revised Manuscript Received November 29, 1993

Polysilane polymers[1] display an intense electronic absorption band in the ultraviolet region 300–400 nm, which is assigned to a σ–σ^* electronic transition[2] involving extensive delocalization of electrons along the silicon backbone. The energy of the electronic absorption is strongly correlated with the conformation of the polymer chain, similarly to the π–π^* transition in well-known π-conjugated polymers such as polydiacetylene[3] and polythiophene.[4] Many dialkylpolysilanes[5] undergo either a gradual or abrupt shift of the absorption band to longer wavelength as temperature is lowered, associated with a disorder–order transformation. To date, considerable efforts have been devoted to disclosing the nature of abrupt thermochromic transition, especially in the symmetric dialkylpolysilanes. Polymers $(n\text{-alkyl}_2\text{Si})_n$, where n-alkyl = hexyl, n-heptyl, and n-octyl, all exhibit abrupt thermochromism in the solid state accompanied with a phase transition from hexagonal columnar liquid-crystalline forms to an all-trans crystalline form.[6] The driving force for inducing this transition has been attributed to side-chain crystallization, which occurs simultaneously. However, recent investigations[7] on poly[(5-ethoxypentyl)-alkylsilane]s, which undergo abrupt thermochromism simultaneously with a first-order-like phase transition without side-chain crystallization, have led us to a different viewpoint about the nature of this thermochromic behavior.

To further reveal the role of the side chain on the thermochromism of polysilanes, the series of poly(n-alkylmethylsilane)s containing a various number of carbon atoms in the side groups, $(\text{RMeSi})_n$ (R = n-butyl to n-dodecyl), was synthesized via the conventional Wurtz-coupling polymerization (Table 1).[8] The temperature-dependent UV spectra of poly(n-butylmethylsilane) [$(\text{BuMeSi})_n$] and poly(n-pentylmethylsilane) [$(\text{PenMeSi})_n$] films (Figure 1) showed only a continuous bathochromic shift as the temperature was decreased, but polymers with six or more carbon atoms in the side chain all displayed an abrupt thermochromic transition. Moreover, the onset temperature[9] of the discontinuous thermochromism was found to increase as the length of the alkyl chain increased, although with some alternation leading to a zigzag profile (Figure 2).[10,11] The thermochromic transition for this family of polysilanes is also reflected in their thermal properties (Figure 3). In $(\text{BuMeSi})_n$, the DSC thermogram displayed only a second-order transition corresponding to the glass transition. As the chain length increases, a first-order transition occurring simultaneously with the thermochromism is observed, with ΔH increasing from pentyl- to heptyl-substituted polysilanes. Wide-angle X-ray diffraction powder patterns of these polymers show that they are all amorphous, both above and below the thermochromic transition temperature.

Table 1. Thermochromic Transition for the Series of $(n\text{-alkylMeSi})_n$ Films[a]

polymer $(\text{RMeSi})_n$	onset temp T_0 (°C)	$\lambda_{\max}$ (nm)		$M_w \times 10^{-3}$ [d]
		α[b]	β[c]	
Bu	none	302	313	376, 19.9
Pen	none	302	322	731, 107, 23.7
Hex	−23	298	325	179, 18.4
Hep	−10	298	324	356
Oct	−1	301	330	594, 31.5
Non	−5	301	330	741, 41.7
Dec	16	301	330	536
Undec	12	302	325	228, 14.9
Dodec	26	302	328	697

[a] UV spectra were taken from films cast on quartz, at a cooling rate of ca. 2 °C/min. [b] UV absorption at 26 °C. [c] UV absorption peak after red shifting is complete. [d] M_w were determined by GPC, relative to polystyrene standards.

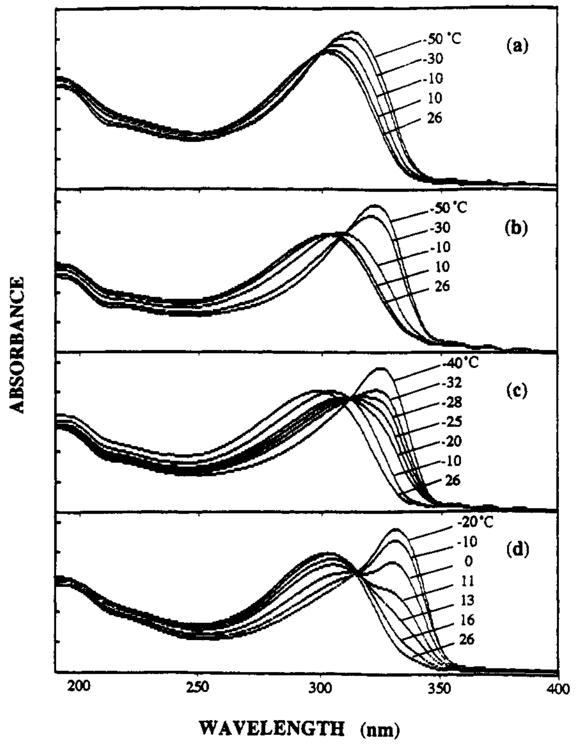

Figure 1. Temperature-dependent UV spectra of (a) $(\text{BuMeSi})_n$, (b) $(\text{PenMeSi})_n$, (c) $(\text{HexMeSi})_n$, and (d) $(\text{DecMeSi})_n$ film at a cooling rate of ca. 2 °C/min.

As the polymers are cooled through the transition temperature, they probably adopt a more extended conformation with a greater number of all-trans segments along the polymer chain. Support for this interpretation is provided by the variable-temperature ^{29}Si CPMAS NMR spectra of $(\text{DodecMeSi})_n$ (Figure 4). As this polymer goes through the thermochromic transition, a new downfield resonance appears and grows in intensity. A more extended polymer structure should lead to deshielding of the silicon nucleus,[12] exactly as observed.

Our results are nicely accounted for by the model elaborated by Schweizer.[13] According to this theory, the thermochromic phenomena can generally arise from the dispersion interaction between delocalized electrons along the polymer backbone and the surrounding polarizable "medium", which can be the pendant side chains, neighboring polymer chains, or solvent molecules. In solid poly(di-n-alkylsilane)s, the hydrocarbon side chains probably play the most important role. The transition between the ordered and disordered conformation is induced by a competition between the dispersion interaction for fully ordered chain segments, V_D, and the rotational defect energy, ϵ. The ratio V_D/ϵ controls the type of thermochromic behavior, which may include either an abrupt or continuous transition.

0024-9297/94/2227-0629$04.50/0

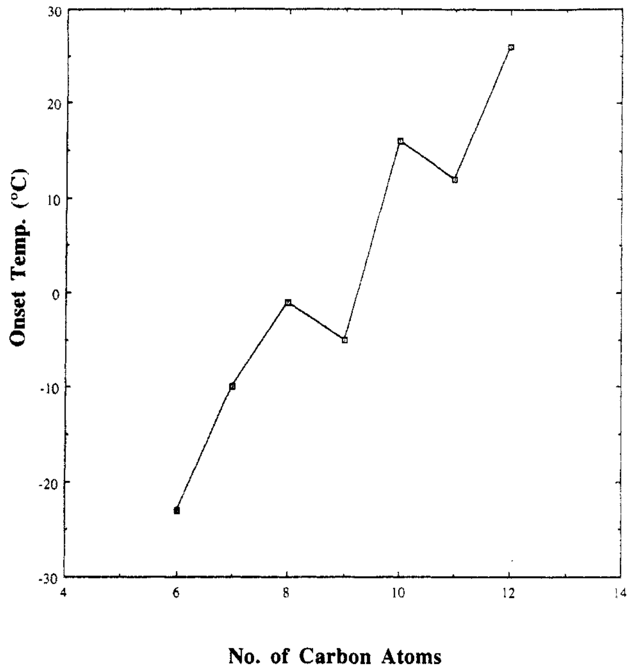

Figure 2. Onset temperature of an abrupt transition for (n-alkylMeSi)$_n$ in solid state vs the number of carbon atoms in the alkyl substituent.

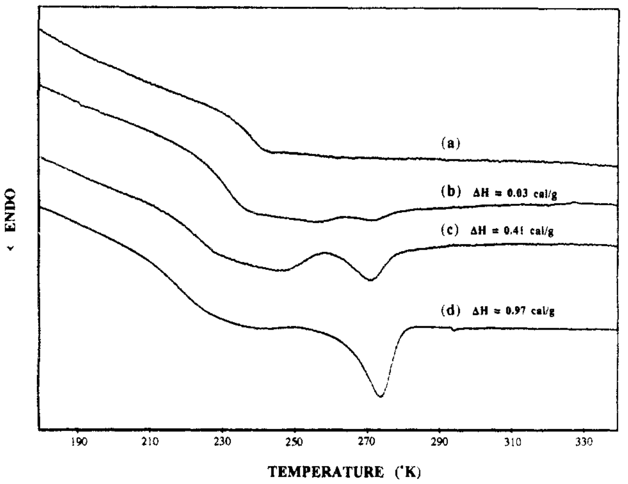

Figure 3. DSC thermograms of (a) (BuMeSi)$_n$, (b) (PenMeSi)$_n$, (c) (HexMeSi)$_n$, and (d) (HepMeSi)$_n$ at a heating rate of 20 °C/min with respective endothermic enthalpies. Transition temperatures were reproducible within 1 °C.

In (n-alkylMeSi)$_n$, the dispersion interaction between the polarizable side chains and the polysilane backbone appears to be crucial. In (BuMeSi)$_n$, the short side chain interacts only weakly with the polysilane chromophore, so that only a gradual bathochromic shift is observed with decreasing temperature. This shift corresponds to "weak coupling", with a small value of V_D/ϵ. The (PenMeSi)$_n$ polymer indicates an intermediate case without abrupt thermochromism; variable-temperature UV spectra were examined carefully and showed no abrupt transition but a rapid red shifting with decreasing temperature in the range of −10 to −30 °C, compared to a gradual shift in (BuMeSi)$_n$. In (HexMeSi)$_n$, greater polarizability induced by the longer hexyl substituent increases V_D/ϵ to the point where a discontinuous transition is triggered ("strong coupling"). The polarizability of the side chain increases with the number of carbon atoms, leading to larger values of V_D/ϵ and a higher onset temperature.

Acknowledgment. This research was supported by the Office of Naval Research under Contract No. N00014-92-J-1443.

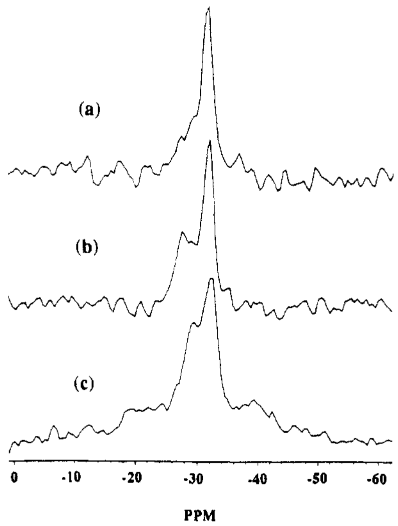

Figure 4. Variable-temperature 59.59-MHz ^{29}Si CPMAS solid-state NMR spectra of (DodecMeSi)$_n$ at (a) 40, (b) 30, and (c) 10 °C.

References and Notes

(1) Reviews: (a) Miller, R. D.; Michl, J. *J. Chem. Rev.* **1989**, *89*, 1359. (b) West, R. In *Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 1207.
(2) (a) Klingensmith, K. A.; Downing, J. W.; Miller, R. D.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 7438. (b) Harrah, L. A.; Zeigler, J. M. *Macromolecules* **1987**, *20*, 601.
(3) (a) Patel, G. N.; Witt, J. D.; Khanna, Y. P. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1383. (b) Plachetta, C.; Rau, N. O.; Schulz, R. C. *Mol. Cryst. Liq. Cryst.* **1983**, *96*, 141. Chance, R. R.; Patel, G. N.; Witt, J. D. *J. Chem. Phys.* **1979**, *71*, 206.
(4) (a) Inganas, O.; Salanek, W. R.; Osterholm, J. E.; Laakaso, J. *Synth. Met.* **1988**, *22*, 395. (b) Roux, C.; Leclerc, M. *Macromolecules* **1992**, *25*, 2141.
(5) (a) Klemann, B.; Robert, R.; Koutsky, J. A. *Macromolecules* **1993**, *26*, 1042. (b) Miller, R. D.; Wallraff, G. M.; Baier, M.; Cotts, P. M.; Shukla, P.; Russell, T. P.; De Schryver, F. C.; Declercq, D. *J. Inorg. Organomet. Polym.* **1991**, *1*, 505. (c) Wallraff, G. M.; Baier, M.; Miller, R. D.; Rabolt, J. F.; Hallmark, V.; Cotts, P. M.; Shukla, P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30*, (2), 245. (d) Trefonas, P., III; Damewood, J. R.; West, R.; Miller, R. D. *Organometallics* **1985**, *4*, 1318.
(6) (A) Schilling, F. C.; Bovey, F. A.; Zeigler, J. M. *Macromolecules* **1986**, *19*, 2309. (b) Rabolt, J. F.; Hofer, D.; Miller, R. D.; Fickes, G. N. *Macromolecules* **1986**, *19*, 611.
(7) Yuan, C. H.; West, R. *Macromolecules* **1993**, *26*, 2645.
(8) West, R.; David, L. D.; Djurovich, P. I.; Stearley, K. L.; Srinivasan, K. S. V.; Yu, H. *J. Am. Chem. Soc.* **1981**, *103*, 7352.
(9) The onset temperature was defined as that temperature at which a significant UV shift, ca. 2 nm, is first observed upon cooling the polymer film by 1 °C.
(10) In order to examine the effect of molecular weight on the thermochromic transition, (OctMeSi)$_n$ which had a bimodal M_W distribution was separated by fractional precipitation from toluene with 2-propanol into a high M_W fraction, $M_W = 5.4 \times 10^5$, and a low M_W fraction, $M_W = 4.2 \times 10^3$. The UV vs temperature plots for the two fractions showed no significant difference.
(11) Poly(n-hexylmethylsilane) [(HexMeSi)$_n$] represents an intermediate case in which the wavelengths of the absorption bands before and after the triggering of an abrupt thermochromic transition are quite close, so the onset temperature is not easily determined. Previous studies of (HexMeSi)$_n$ films report a gradual thermochromic shift but not a discontinuous transition. See: Miller, R. D.; Wallraff, G. M.; Baier, M.; Cotts, P. M.; Shukla, P.; Russell, T. P.; De Schryver, F. C.; Declercq, D. *J. Inorg. Organomet. Polym.* **1991**, *1*, 505.
(12) (a) Schilling, F. C.; Lovinger, A. J.; Zeigler, J. M.; Davis, D. D.; Bovey, F. A. *Macromolecules* **1989**, *22*, 3055. (b) Tonelli, A. E.; Gomez, M. A.; Tanaka, H.; Schilling, F. C.; Cozine, M. H.; Lovinger, A. J.; Bovey, F. A. In *Polymer Characterization*; ACS Symposium Series 227; American Chemical Society: Washington, DC, 1990; pp 409–451.
(13) (a) Schweizer, K. S. *Chem. Phys. Lett.* **1986**, *125*, 118. (b) Schweizer, K. S. *J. Chem. Phys.* **1986**, *85*, 1156, 1176. (c) Schweizer, K. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1986**, *27* (2), 354.