Kinetics of Chain Organization at the Thermochromic Transition of Polysilanes[1]

Takanobu Sanji,[#] Kenkichi Sakamoto, and Hideki Sakurai*,[#]
Department of Chemistry and Organosilicon Research Laboratory, Faculty of Science, Tohoku University, Aoba-ku, Sendai 980-77

(Received October 28, 1997; CL-970832)

Kinetics of the conformational transition of polysilanes was studied by monitoring the time dependent changes in UV absorption. The conformational change is regarded as a process of the crystallization and its time evolution in conformity to the scaling law with three-dimensional growth of the transition.

Poly(di-n-hexylsilane) (PDHS), which is studied in detail, exhibits an abrupt thermochromism in a narrow temperature range both in solution and in the solid state.[2] The absorption maxima of PDHS in the solid state shifts from 365 nm at room temperature to 315 nm above the transition temperature (42 ℃). This unique behavior is originated from the conformational change of the polysilane backbone between hexagonal columnar liquid-crystalline forms and an all-trans crystalline form.[3] The most important point is that the conformational transition of PDHS is accompanied with a well-defined first order phase transition which is made clear by DSC measurement.[3] Therefore, the thermochromic behavior is a good probe for the first order phase transition of polysilane. Although the conformational transition of polysilanes has been studied by a large number of investigators,[4] little is known about the kinetics.[5] We wish to report herein the kinetics of the conformational transition of polysilanes focused on the process of the crystallization by monitoring the time dependent changes in UV absorption.

PDHS was synthesized by the conventional Wurtz-coupling condensation (Mn = 1.8×10^5; Mw/Mn = 2.3). Films of PDHS were prepared by casting a solution of the polymer in benzene onto quartz plates followed by evaporation.[6] The reversible thermochromism of PDHS has a thermal hysteresis and the transition occurred at 42 ℃ in a heating run and at 29 ℃ in a cooling run measured by DSC.[3] In order to study the kinetics of the conformational transition of the polysilane, a polymer film of PDHS was heated at 60 ℃ for several minutes and then quenched by cooling rapidly below the transition temperature. Then the change of UV spectra of the film was measured with a few seconds intervals. A typical example of the observed time-dependent UV spectra is shown in Figure 1. Intensities of the absorption peak of the all-trans low temperature form (365 nm) increased gradually, while those of the high temperature form (315 nm) decreased. During the changes, a clear isosbestic point was observed at 335 nm. Existence of the isosbestic point indicates the coexistence of well-defined two phases. Thus the conformational transition must be a cooperative interconversion of the two phases.

In these measurement the fraction of all-trans form ($X(t)$) is given by,

$$X(t) = \frac{I(t) - I(0)}{I(\infty) - I(0)}, \qquad (1)$$

where $I(t)$ is the intensity at 365 nm at the time t. The resulting absorption intensities of the trans fraction ($X(t)$) versus time at 20, 25 and 27 ℃ are shown in Figure 2. The growth rate of the trans fraction increased with decreasing the quenching temperature.[7]

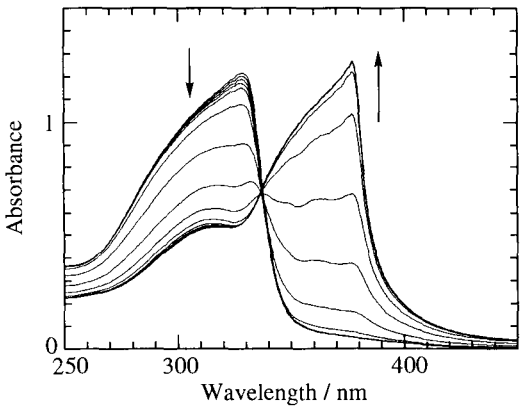

Figure 1. Time-dependent UV spectra of poly(di-n-hexylsilane) in the solid state measured with 15 seconds intervals when quenched from 60 °C to 25 °C.

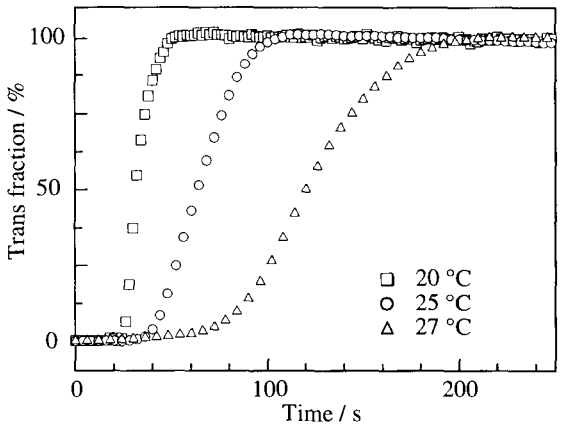

Figure 2. Time dependence of the trans fraction of poly(di-n-hexylsilane) quenched from 60 °C to 20 °C (□), 25 °C (○), and 27 °C (△).

A key concept of understanding the phase transitions is the scaling law.[8] According to the scaling law, the curves representing the growth of the ordered species formed by the change of controlling factors must have a universal shape when expressed in terms of a scaled time. In this study the characteristic scaling time ($t_{1/2}$) for the transformation was defined by the relation of $X(t_{1/2})$ = 1/2 for each quenching temperature. As shown in Figure 3, the trans fractions at each temperature fit nicely to a universal shape when plotted against the scaled time (τ

Copyright © 1998 The Chemical Society of Japan

$= t/t_{1/2}$).

In the scaling law, $X(t)$ is expressed as a function of nucleation rate (I) and domain-wall growth rate (v). The simplest picture of the nucleation and the growth of domain-wall that satisfies a required scaling is the following. When the temperature of a system is instantaneously lowered below the transition temperature, the micro grains of the stable phase formed randomly at a constant rate, I. Since I is time independent, I decreases with the fraction of metastable phase remaining, $1\text{-}X(t)$. Once formed, the grain grows isotropically with a constant domain-wall growth rate, v. Since the model is characterized by two parameters I and v, it follows that there exists a single characteristic scaling time. Accordingly, the time dependency of X must be universal when expressed in terms of the scaled time. Then an explicit expression for $X(t)$ was given by,

$$X(t) = 1 - \exp\left[-D\int_0^t I[vt']^d dt'\right] \qquad (2)$$

$$D = 2,\ \pi,\ 4\pi/3 \quad \text{for } d = 1,\ 2,\ 3$$

where d is the dimension of growth and t' is a time after the nucleation.[9,10] For the conformational transition of polysilanes the following universal scaling function was derived from eq. 2, where τ is the scaled time mentioned above.

$$X(\tau) = 1 - \exp(-\ln 2 \cdot \tau^d) \qquad (3)$$

This scaled theoretical curve is compared with the experimental data in Figure 3. The theoretical curve for $d = 3$ is in good agreement with the experimental points.[11,12]

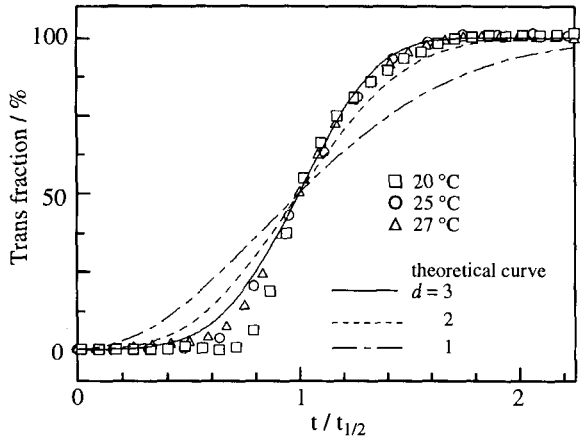

Figure 3. Universal scaled curves plotted in terms of the characteristic scaled times for the transformation of poly(di-n-hexylsilane) in the solid state.

There are some problem for the model applied for the analysis of our measurement. It should be noticed that there exists the time scale and *length (or spatial) scale* in the scaling function.[13] If additional measurement of the length scaling could be made, more detailed microscopic model of the phase transition for the polysilane would be discussed. Nevertheless, the mechanism of the phase transition for this polysilane must be independent of the temperature covered in this measurement, *i.e.*, the thermochromism of polysilanes is regarded as a process of the crystallization and its time evolution in conformity to the scaling law with three-dimensional growth of the transition.

We thank Professor K. Ono of Ibaraki University for valuable discussion. We are also grateful for the financial support of the Ministry of Education Science and Culture of Japan (Specially Promoted Research No. 02102004). T. S. thanks the Japan Society for Promotion of Science for the Fellowships for Junior Scientist.

References and Notes

\# Present address: Department of Industrial Chemistry, Faculty of Science and Technology, Science University of Tokyo, 2641 Yamazaki, Noda, Chiba 278

1 Chemistry of Organosilicon Compounds 351.

2 For reviews of polysilane, see: a) R. West, *J. Organomet. Chem.*, **300**, 327 (1986). b) R. D. Miller and J. Michel, *Chem. Rev.*, **89**, 1359 (1989).

3 a) R. D. Miller, D. Hofer, J. Rabolt, and G. N. Fickes, *J. Am. Chem. Soc.*, **107**, 2172 (1985). b) F. C. Schilling, F. A. Bovey, and J. Zeigler, *Macromolecules*, **19**, 2309 (1986). c) J. Rabolt, D. Hofer, R. D. Miller, and G. N. Fickes, *Macromolecules*, **19**, 611 (1986).

4 a) H. Kuzmay, J. F. Rabolt, B. L. Farmer, and R. D. Miller, *J. Chem. Phys.*, **85**, 7413 (1986). b) E. K. Karikari, A. J. Greso, B. L. Farmer, R. D. Miller, and J. F. Rabolt, *Macromolecules*, **26**, 3937 (1993). c) C. -H. Yuan and R. West, *Macromolecules*, **26**, 2645 (1993). d) C. -H. Yuan and R. West, *Macromolecules*, **27**, 629 (1994).

5 Preliminary results of this paper were presented at "*Sendai International Symposium on the Frontiers of Oganosilicon Chemistry*", Sendai, Japan, November 4-6, 1994, Abstract p 198. Very recently, related work has been reported: M. M. Despotopoupou, C. W. Frank, R. D. Miller, and J. F. Rabolt, *Macromolecules*, **29**, 5797 (1996).

6 Recently, restrictions of the conformational change of PDHS in ultrathin spincast films less than 150 Å thick have been reported; M. M. Despotopoupou, C. W. Frank, R. D. Miller, and J. F. Rabolt, *Macromolecules*, **28**, 6687 (1995).

7 When the quenching temperature was 28 °C, very close to the transition temperature, the peak corresponding to the all-trans forms increased very slowly. Even after several hours, the peak did not reach to the 100 % level.

8 a) Y. Yamada, N. Hamaya, J. D. Axe, and S. M. Shapiro, *Phys. Rev. Lett.*, **53**, 1665 (1984). b) M. K. Phani, J. L. Lebowitz, M. H. Kalos, and O. Penorose, *Phys. Rev. Lett.*, **45**, 366 (1980). c) P. S. Sahni, J. D. Gunton, *Phys. Rev. Lett.*, **45**, 369 (1980). d) Y. C. Chou and W. I Goldburg, *J. Phys. Chem.*, **85**, 1972 (1981).

9 This equation was derived independently by A. N. Kolmogorov, (*Bull. Acad Sci. U. S. S. R. Phys. Ser.*, **3**, 355 (1937).) and M. Avrami, (*J. Chem. Phys.*, **7**, 1103 (1939). and **8**, 212 (1940). and **9**, 177 (1941).)

10 It should be noted that this formulation only works when the nucleation and growth are governed by a single characteristic time.

11 The growth dimension of the crystallization is further supported by analyses of the Avrami equation which is developed for polymer crystallization. All the growth of trans fractions were fit the Avrami equation of homogeneous nucleation. At each quenching temperature the dimension of the nucleation was calculated to be 3.

12 The experimental points appeared not to fit the theoretical curve very well especially at the initial stage ($t/t_{1/2}<1.0$). The process of the phase transition at the lower quenching temperature was very rapid, so that the analyses of the initial stage for the phase transition become increasingly difficult. In the initial stage for the phase transition, the length scale could be influenced by not only the average size of the domain but also thickness of the domain-wall, while the average size of the domain is a factor governing the length scale with the negligible contribution of the thickness of the domain-wall after appropriate time.[13]

13 a) J. G. Amar, F. E. Sullivan, and R. D. Mountain, *Phys. Rev. B.*, **37**, 196 (1988). b) M. Takenaka and T. Hashimoto, *J. Chem. Phys.*, **96**, 6177 (1992).