

Solid-State ^{29}Si NMR Analyses of the Structure and Dynamics of Solid Poly(di-*n*-alkylsilane)s

Hironori Kaji and Fumitaka Horii

Solid-state ^{29}Si NMR analyses of the solid structure and dynamics have been performed for poly(di-*n*-butylsilane) with the order-disorder transition at 76 °C. ^{29}Si chemical shift anisotropy (CSA) spectra are measured with an ultraslow magic angle spinning at a rate less than 100 Hz. Almost rigid CSA spectra for the 7/3 helical structure are observed below the transition temperature. In contrast, axially symmetric CSA spectra with different principal values appear above the transition temperature, suggesting the onset of the rotational motion around the molecular chain axis with trans-rich conformation. The changes of the conformation and dynamics around the transition are also discussed for other poly(di-*n*-alkylsilane)s such as poly(dimethylsilane) and poly(di-*n*-hexylsilane).

Keywords: Poly(di-*n*-alkylsilane)s / CPMAS NMR / Chemical shift anisotropy / Ultraslow MAS / Solid structure / Dynamics

Polysilanes are a new class of polymers which contain only silicon atoms in the backbone. They have been attracting much interest because of their interesting electronic and chemical properties, such as photoconductivities, and nonlinear optical properties. These properties are dominated by σ -delocalization of electrons along the silicon backbone and thus considered to be strongly dependent on the chain conformation and molecular motion. For this reason, we have been particularly interested in the characterization of the conformational structure and dynamics of the silicon-based materials on the molecular level. Among them, poly(di-*n*-alkylsilane)s are known to have the order-disorder transition and the liquid crystalline state has recently been found above this transition temperature. In this report, we investigate the

solid structure and dynamics of poly(di-*n*-butylsilane) (PDBS), poly(dimethylsilane) (PDMS) and poly(di-*n*-hexylsilane) (PDHS) by solid-state ^{29}Si NMR analyses, in particular around the order-disorder transition temperature.

PDBS and PDHS, which were kindly provided by Shin-Etsu Chemical Co., Ltd, were isothermally annealed at 100 °C for 10 hr in vacuum. DSC measurements were performed on TA Instruments DSC-2910. Solid-state ^{29}Si NMR measurements were conducted on JEOL JNM-GX400 and Chemagnetics CMX-400 spectrometers both operating under a static magnetic field of 9.4 T. ^1H and ^{29}Si field strengths $\gamma B_1/2\pi$ were 50 - 59.5 kHz. The contact time for the CP process was 3 and 10 ms for the ordered and disordered phases, respectively. The rate of sample spinning was set

FUNDAMENTAL MATERIAL PROPERTIES —Molecular Dynamic Characteristics—

Scope of research

The Research activities in this subdivision cover structural studies and molecular motion analyses of polymers and re-lated low molecular weight compounds in the crystalline, glassy, liquid crystalline, solution, and frozen solution states by high-resolution solid-state NMR, dynamic light scattering, electron microscopy, and so on, in order to obtain basic theories for the development of high-performance polymer materials. The processes of biosynthesis, crystallization, and higher-ordered structure formation are also studied for bacterial cellulose.



Prof
HORII Fumitaka
(D Eng)



Assoc Prof
TSUNASHIMA
Yoshisuke
(D Eng)



Instr
KAJI Hironori
(D Eng)



Assoc Instr
HIRAI Asako
(D Eng)



Techn
OHMINE
Kyoko

Guest Scholar

SHEN, Yimin (Assoc Prof, DSci)

Students

ISHIDA, Hiroyuki (DC)

KAWANISHI, Hiroyuki (MC)

KUWABARA, Kazuhiro (MC)

TAI, Toshihiro (MC)

MASUDA, Kenji (MC)

HATTORI Kimihiko (UG)

TAJIRI Kouji (UG)

ZHENG Jianming (RS)

to 4 kHz. ^{29}Si chemical shifts were expressed as values relative to tetramethylsilane (Me_4Si) by using the resonance line at -34 ppm for PDMS crystals as an external reference.

The order-disorder transition temperatures determined for PDMS, PDBS and PDHS by DSC were 157.8 °C, 75.9 °C and 44.4 °C, respectively. Figure 1 shows CP/MAS ^{29}Si NMR spectra of PDBS at different temperatures. The upfield and downfield resonance lines, which correspond to the ordered and disordered phases, are observed respectively below and above 70 °C, as is already reported by Schilling et al [1]. X-ray diffraction analyses revealed that PDBS has 7/3 helical structure in the ordered state [1]. Considering the γ gauche effect, the higher chemical shift value in the disordered phase suggests that the chain conformation approaches to the planar *trans* conformation in this phase. In contrast, an upfield shift from -21.3 ppm at room temperature to -25.8 ppm at 80 °C is observed for PDHS, suggesting that the *trans* conformation in the ordered phase changes some helical structure in the disordered phase. No chemical shift change is observed for PDMS between room temperature and 200 °C within the experimental error.

Table 1 shows ^{29}Si spin-lattice relaxation times (T_1) for PDBS at different temperatures, measured by the CPT1 pulse sequence. T_1 values in the disordered phase are much shorter than those in the ordered phase. Such an evident difference in T_1 indicates the onset of the enhanced molecular motion in the disordered phase.

Table 1 Chemical shift and T_1 for PDBS.

Temperature/°C	rt	60	80	100
Chemical shift / ppm	-26.1	-25.0	-23.0	-22.3
T_1 / s	240	300	11	10

In order to characterize the detail of the molecular motion in the disordered phase, the spectra reflecting the ^{29}Si chemical shift anisotropy (CSA) are measured for PDBS at different temperatures. Figure 2 shows the ^{29}Si CSA spectra obtained under an ultraslow magic angle spinning at a rate less than 100 Hz, which is insensitive to CSA lineshapes. Typical CSA powder patterns, which reflect the principal values, σ_{11} , σ_{22} , and σ_{33} , of the chemical shift tensor in the rigid state are observed below the transition temperature. Such CSA spectra suggest that the molecular motion of the main chain is frozen in a time scale of 10^{-2} s. In contrast, axially symmetric CSA spectra are observed above the transition temperature. Assuming that σ_{11} corresponds to the molecular chain axis, these axially symmetric CSA spectra suggest that PDBS chains undergo the rotational motion around the chain axis with the frequency above 10^3 Hz. This result is consistent with the result of X-ray diffraction [1] which reveals the hexagonal packing in the disordered phase. Such rotational

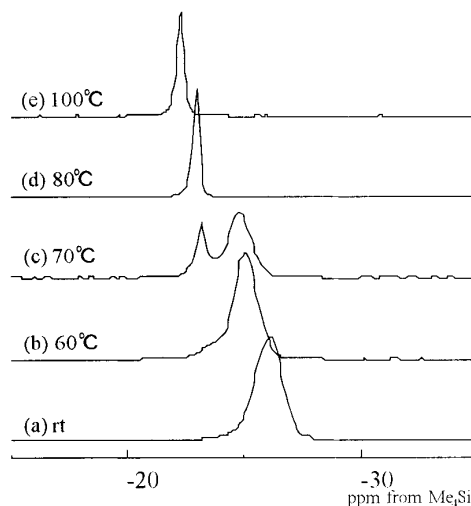


Figure 1. 79.6 MHz CP/MAS ^{29}Si NMR spectra of solid PDBS at various temperatures. The spinning rate is 4 kHz.

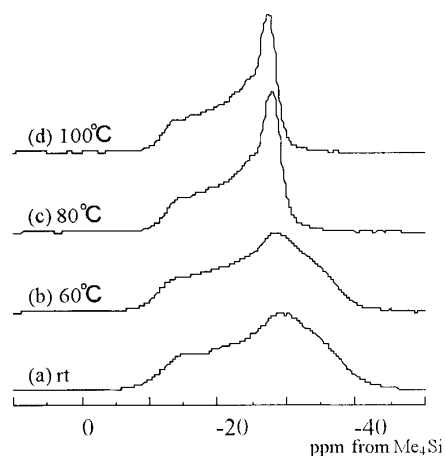


Figure 2. Ultraslow-MAS ^{29}Si CSA spectra of PDBS at various temperatures. The spinning rate is less than 100 Hz.

motion may be similar to the motion observed for *n*-alkane [2] in the hexagonal phases.

The analyses of T_1 and CSA powder patterns for PDMS and PDHS also suggest some enhanced molecular motion in the disordered phase. More detailed characterization of these polymers are in progress.

References

- Schilling F C, Lovinger A J, Zeigler J M, Davis D D and Bovey F A, *Macromolecules*, **22**, 3055 (1989).
- Kitamaru R, Horii F, Nakagawa M, Takamizawa K, Urabe Y and Ogawa Y, *J. Molec. Struct.*, **355**, 95 (1995).