Proton Magnetic Relaxation and Molecular Motion in Crystalline Tetramethylsilane

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Synopsis. The molecular motion in the three modifications of tetramethylsilane was studied by the spin-lattice relaxation time measurements. The activation parameters for the methyl group reorientation, overall molecular tumbling, and the molecular self-diffusion were determined in each phase. A possible correlation between these parameters and the stability of the plastic phase was pointed out.

In our previous NMR and heat capacity measurements we established the phase relation in the crystalline tetramethylsilane, $(CH_3)_4Si$, which is hereafter abbreviated as TMS.[1,2] There are three crystalline modifications in TMS. The α phase is a metastable plastic crystal which melts at 165.9 K and, on cooling down to about 159 K, changes spontaneously into the β phase which melts at 171.0 K. The β phase can be supercooled down to very low temperatures, but transforms, on heating, into another phase, the γ phase, at about 118 K. The γ phase is the most stable phase over the whole temperature range of the crystalline state. It melts at 174.1 K. We also obtained the gross feature of the dynamic structure of the β and the γ phases of TMS by proton magnetic resonance,[1] but were not able to derive the quantitative information about the molecular motional modes in each of the three phases. The present study therefore was undertaken to investigate the characteristics of the molecular motions being excited successively in TMS with extensive measurements of the spin-lattice relaxation times in the laboratory and the rotating frames, T_1 and $T_{1\rho}$. The correlation between the molecular motion and the stability of the unique plastic phase in TMS will also be discussed.

Experimental

TMS from commercial source (Merck) was purified by vacuum distillation, outgassed by the freeze-pump-thaw technique and sealed under vacuum in a glass ampule. The NMR relaxation experiments were done at 15.0 MHz with a Bruker CXP 4-60 MHz pulsed NMR spectrometer. The T_1 was measured by the saturation-90° method. The $T_{1\rho}$ values were measured using the spin-locking method with a rotating r.f. magnetic field, B_1, of 0.7 mT for the β and the γ phases and also of 0.2 and 1.0 mT for the α phase. The estimated error in both relaxation times was less than ±4%. Temperatures were controlled to within ±0.1 K and the accuracy of the temperature measurement was better than ±0.3 K.

Results and Discussion

α Phase. Figure 1 shows the temperature dependence of T_1 and $T_{1\rho}$ in the metastable plastic α phase. The slope in T_1 below about 165 K leads to an activation energy E_a of 5.5±1.3 kJ mol^{-1} which corresponds to the overall molecular tumbling or reorientation. Above about 165 K another motion is excited. This motion shows B_1 independence of $T_{1\rho}$

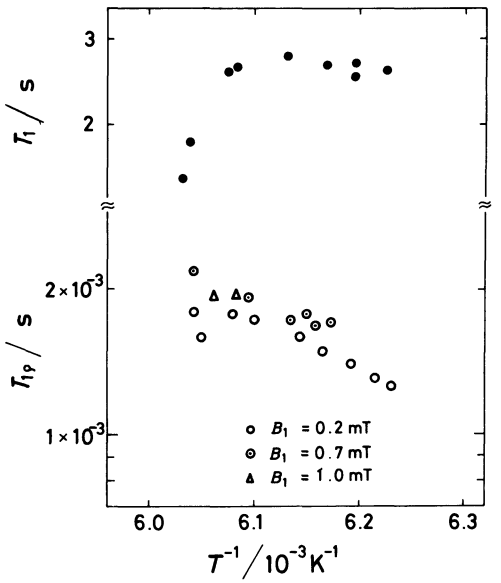

Fig. 1. Temperature dependence of T_1 (●) and $T_{1\rho}$ at B_1=0.2 mT (○), 0.7 mT (◉), and 1.0 mT (△) at the Zeeman frequency, 15.0 MHz for the α phase.

Table 1. Activation Parameters for Overall Molecular Tumbling and Self-Diffusion in Some Plastic Crystals

	$(CH_3)_4C$	$(CH_3)_4Si$	$(CH_3)_3CCl$	$(CH_3)_3CBr$	$(CH_3)_3CNO_2$	CCl_3CF_3
E_a^r/kJ mol^{-1}	3.68	5.5	4.26	13.6	6.8	5.9
E_a^d/kJ mol^{-1}	33.9	20.4	33.5	51.8	46.5	35
E_a^d/E_a^r	9.2	3.7	7.9	3.8	6.8	5.9
Reference	a)	This work	b)	Ref. 4	Ref. 6	c)

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Table 2. Activation Energies, E_a, and Inverse Frequency Factors, τ_0, for Molecular Motions in α, β, and γ Phases of Tetramethylsilane

Motion	Parameter	Phase		
		α phase	β phase	γ phase
Methyl reorientation	E_a/kJ mol^{-1}	—	6.44±0.19	6.92±0.09
	τ_0/s	—	$(4.72\pm0.80)\times10^{-13}$	$(3.63\pm0.31)\times10^{-13}$
Overall molecular tumbling	E_a^r/kJ mol^{-1}	5.5±1.3	31.9±0.9	43.0±1.6
	τ_0^r/s	—	$(5.1\pm2.6)\times10^{-17}$	$(2.6\pm1.6)\times10^{-19}$
Self-diffusion	E_a^d/kJ mol^{-1}	20.4±1.6	—	—

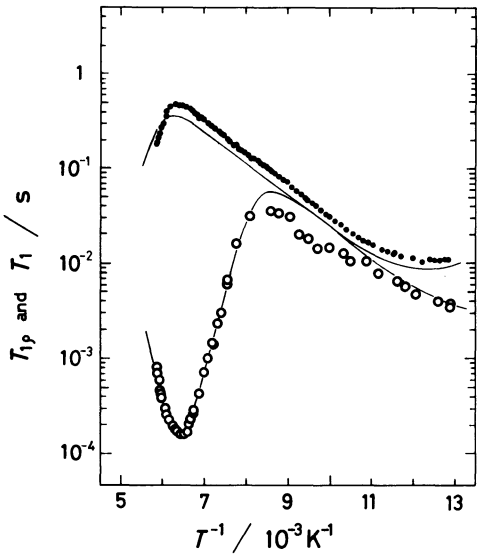

Fig. 2. Temperature dependence of T_1 (●) and $T_{1\rho}$ (○) at B_1=0.7 mT for the β phase; the Zeeman frequency is 15.0 MHz. The solid lines indicate the theoretical relaxation times.

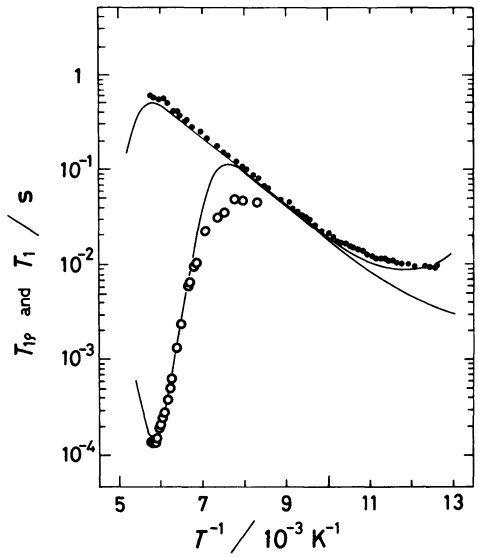

Fig. 3. Temperature dependence of T_1 (●) and T_ρ (○) at B_1=0.7 mT for the γ phase; the Zeeman frequency is 15.0 MHz. The solid lines indicate the theoretical relaxation times.

and causes to increase $T_{1\rho}$ values monotonously on heating. The slope of the $T_{1\rho}$ gives the activation energy, E_a=20.4±1.6 kJ mol^{-1}, which is certainly attributed to molecular self-diffusion.

The activation energies for the overall molecular reorientation, E_a^r, and for molecular self-diffusion, E_a^d, in some typical plastic crystals which were determined by NMR methods are listed in Table 1 together with the ratio E_a^d/E_a^r for each substance. The values of this ratio are in the range between 4 and 12 for usual plastic crystals.[3] However the values of TMS and $(CH_3)_3CBr$ are somewhat small compared with other plastic crystals; they are 3.7 and 3.8, respectively. It is remarked that the α phase of TMS is metastable as mentioned above and $(CH_3)_3CBr$ has two plastic phases.[4] It is also noted that in $(CH_3)_3CCN$ no plastic phase exists and overall molecular tumbling has not been recognized.[5] So we assume to be $E_a^r \gg E_a^d$ at a moment then we get $E_a^d/E_a^r \ll 1$ in the case $(CH_3)_3CCN$. These findings strongly suggest that this ratio is closely related to the stability of plastic phase in globular molecular crystal, giving probably a new criterion for the plastic crystal.

β and γ Phases. The relaxation data in these two phases are shown in Figs. 2 and 3, indication that the gross feature of the dynamics of the molecules is quite similar in both phases. We attributed the minima in T_1 near 80 K to the methyl group reorientation, and the minima in $T_{1\rho}$ at about 155 K (in β phase) and 170 K (in γ phase) to the overall molecular tumbling motion. Analyses of these relaxation data by a usual procedure[6,7] lead to the activation parameters for these two kinds of motions as recorded in Table 2. The solid lines in Figs. 2 and 3 show the theoretical relaxation times reproduced using the parameters in Table 2.

Although we ascribed the minima in T_1 near 80 K in the β and γ phases to the methyl group reorientation, a possibility that an anisotropic molecular rotation or reorientation of "rigid" molecule governs the relaxation at low temperatures cannot be ruled out. Our model calculation predicts, for example, that the axial rotation of $(CH_3)_3C$-group about one C–C bond gives the T_1 minimum which is only 5% shorter than that due to independent reorientation of the individual methyl groups. Therefore, we cannot distinguish these different mechanisms at the present stage without detailed structural data.

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