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Polymorphism in Solid $(CH_3)_3CCl$ as Studied by the Method of Differential Thermal Analyses and Nuclear Magnetic Resonance

Sachie OHTANI and Tooru HASEBE*

Department of Chemistry, Faculty of Education,
Fukushima University, Matsukawa-machi, Fukushima 960-12

A differential thermal analysis was performed on solid $(CH_3)_3CCl$ and a new solid phase was found at saturated vapor pressure of the sample. This phase exists between 217.7 K and 219.5 K. Temperature dependence of the ^{1}H-NMR free induction decay time, T_2^*, shows the onset of a new molecular motion in this phase.

Many grobular molecules have plastic crystalline phases[1] below their melting points. 2-Chloro-2-methylpropane, $(CH_3)_3CCl$, is one of such grobular molecules, and has been studied e.g. by calorimetric measurements,[2,3] dielectric measurements,[4] X-ray diffraction,[5,6] neutron scattering,[7] and nuclear magnetic resonance measurements.[8-11] There are three different solid phases at atmospheric pressure, denoted as phase I, II, and III in order of decreasing temperature. It is interesting to compare the polymorphism with 2-bromo-2-methylpropane. The molecular shape and the electric dipole moment of these two molecules are not so much different, however 2-bromo-2-methylpropane has two plastic phases (phase I and II). Recently the existence of two plastic phases at high pressure on solid $(CH_3)_3CCl$ has been confirmed in dielectric measurements and PVT measurements by Wilmers et al.[12] We had gotton an abnormal differential thermogram which might be an overlapping of two phase transitions at phase transition between phases I and II of solid $(CH_3)_3CCl$ at saturated vapor pressure of the sample before the work reported by Wilmers et al. Then we challenged to clarify this abnormal differential thermogram using high purity sample by a method of differential thermal analysis (DTA) and ^{1}H-NMR measurements.

2-Chloro-2-methylpropane obtained from Wako Pure Chemical Industries, Ltd. was purified by normal distillation (bp 324.0-324.1 K), followed by two stage

vacuum distillation and degassed by normal freeze-pump-thaw technique. The specimen was sealed under vacuum in a glass cell which was specially designed[13] for the DTA and also in a glass ampoule of outside diameter of 10 mm for a nuclear magnetic resonance measurement. No impurities were detected by a gas-chromatographic analysis and by a high resolution ^{1}H-NMR measurement of the neat liquid sample, indicating a purity of better than 99.99%. The differential thermal analysis of this specimen was performed between 89.3 K and 304.2 K using specially constructed apparatus.[14] The control of the cooling and heating rate used was in the range 0.4-1.6 K·min^{-1}.

The temperature dependence of the ^{1}H-NMR free induction decay time, T_2^*, in each solid phase was measured at 15.0 MHz between 93.2 K and 250.8 K using a Bruker CXP 4-60 MHz pulsed NMR spectrometer. The temperature was measured with a chromel-P/constantan thermocouple to an accuracy of ±0.3 K and was controlled to within 0.1 K.

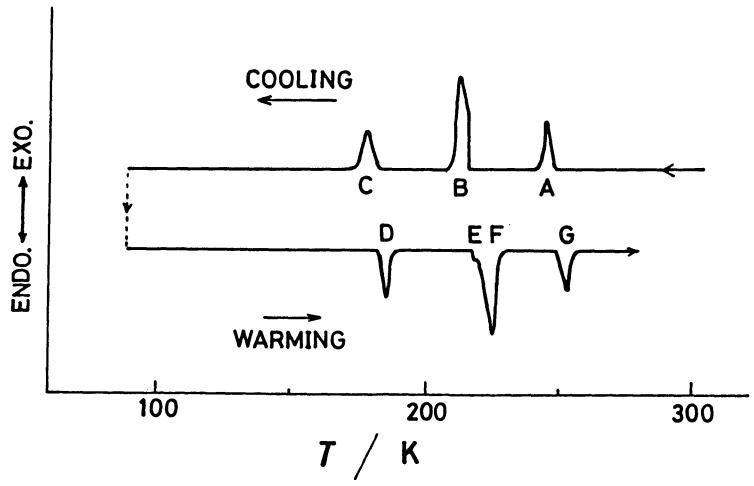

Fig. 1. Differential thermogram of $(CH_3)_3CCl$ showing the phase behavior as function of temperature.

In addition to the three solid forms reported in literatures, we discovered that a forth phase exists between 217.7 K and 219.5 K (between phases I and II in the literatures) at saturated vapor pressure of the sample. Figure 1 shows the differential thermogram to indicate that there are four solid phases. The peak A is the freezing of liquid into phase I. The peak B looks overlapping two phase transitions and that is clarified on heating process by the endothermic peaks E and F. Now we rename them phases I, II, III, and IV in order of decreasing temperature, respectively. The three endothermic peaks (D, E, and F) correspond to phase transitions (IV→III, III→II, and II→I, respectively) and the peak G indicates the melting. To avoid confusion, note that our phases I, III, and IV correspond to

the phases I, II, and III in the literatures, respectively. We therefore find the three solid-solid phase transition points and the melting point, and they are 182.9±0.3 K ($T_{IV\rightarrow III}$), 217.7±0.3 K ($T_{III\rightarrow II}$), 219.5±0.3 K ($T_{II\rightarrow I}$), and 248.2±0.3 K (T_m), respectively.

Figure 2 shows the temperature dependence of the ^{1}H-NMR free induction decay time, T_2^*. The value of T_2^* on phase I changes gradually from 0.4 ms to 2.0 ms with increasing temperature, and this corresponds to the motional narrowing of ^{1}H-NMR line width from ca. 0.02 mT to ca. 0.004 mT. This indicates typically the feature of plastic crystalline phase. On the other hand, the values of T_2^* on phases III and IV indicate the feature of brittle crystalline phase. The value of T_2^* on the

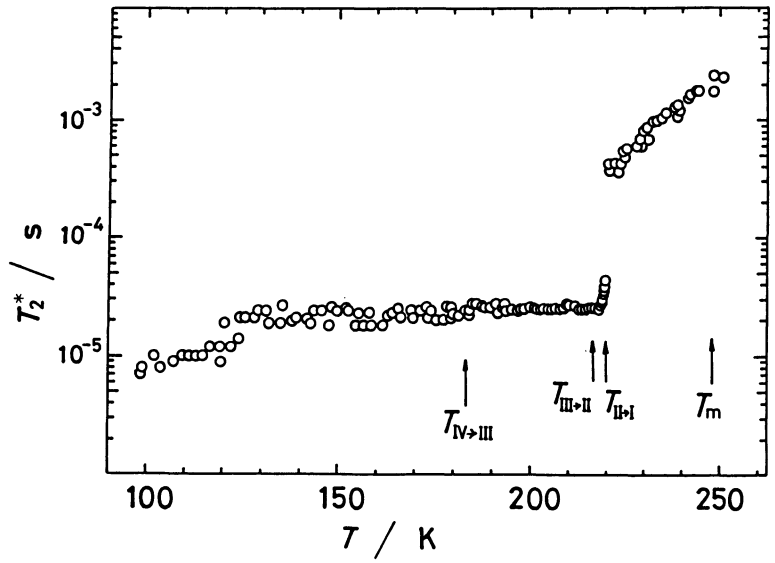

Fig. 2. Temperature dependence of the free induction decay time, T_2^*, in solid $(CH_3)_3CCl$.

new phase II changes from 25 μs to 40 μs (This change corresponds to a change of ^{1}H-NMR line width from ca. 0.3 mT to ca. 0.2 mT.) with increasing temperature. The value of T_2^* on phase II of $(CH_3)_3CCl$ is somewhat small comparing with those of other plastic phases. For example, the value of T_2^* on phase II (which is plastic phase) of $(CH_3)_3CBr$ changes gradually from 0.2 ms to 0.7 ms with increasing temperature. Comparing these values with each other, the value on phase II of $(CH_3)_3CCl$ is smaller than those of $(CH_3)_3CBr$ by a factor of ca. 0.1. If overall molecular reorientation is in full action in phase II of $(CH_3)_3CCl$ as it is in full activity in typical plastic phases, larger value of T_2^* is to be expected as a dipole-dipole interaction is primarily intermolecular. Then the change of T_2^* (i.e. motional narrowing) in phase II indicates the onset of a kind of molecular motions e.g.

hindered molecular tumbling, adding to a methyl and an uniaxial molecular reorientation. As mentioned above the phase II that we confirmed here is different from the forth phase at high pressure previously reported by Wilmers et al.,[12] but we don't discuss any more in this stage. Details of ^{1}H-NMR relaxation times and their analyses will be published elsewhere.

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