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On the Phase Transition of *N*-Methylchloroacetamide

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N-Methylchloroacetamide is one of model compounds of peptide. The infrared and dielectric studies were carried out on the molecular conformation in solution in 1956.[1] Recently Miyazawa has found a phase transition at 38°C by his infrared measurements.[2] He considered that this phase transition is accompanied with the change in the molecular conformation from one of the '*gauche*' type in the low temperature phase (Phase II) to the '*trans*' type in the high temperature phase (Phase I). Later it was found by an X-ray structural study[3] that there are two different kinds of molecules in a monoclinic unit cell of $P2_1/n$ in Phase II: The molecules of one kind assume a planar structure but the others are non-planar. Each kind of molecules assumes '*cis*'-conformation instead of *gauche* form as suggested by previous workers. The N–H···O type hydrogen-bond network exists between the same kind of molecules and extends along the crystalline *c*-axis. The present Note describes the results of the differential thermal analysis (DTA), dielectric measurements, and ^{35}Cl nuclear quadrupole resonance (NQR) studies in an attempt to obtain detailed information with respect to the phase transition.

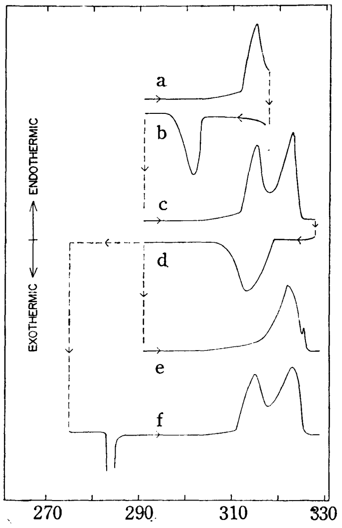

Fig. 1. Differential thermal analysis curves.

The specimen was prepared according to the literature[4] and purified by sublimation under reduced pressure. (mp 45.8±0.2°C; literature value 46°C[1]). Figure 1 shows the DTA curves of the samples having different thermal history. It was found that (1) the specimen which has never been melted or has been stored at room temperature for a long time after melting and freezing undergoes a typical first-order phase transition at 311.6 K which is reversible with a thermal hysteresis effect (curves a, b, and c in Fig. 1), (2) when the specimen is cooled from the melt no phase transition occurs both in cooling and heating directions (curves d and e). The solid phase (Phase III) obtained by cooling the liquid is probably the same as Phase I because their mp and shape and magnitude of the thermal anomaly coincide with each other, (3) Phase

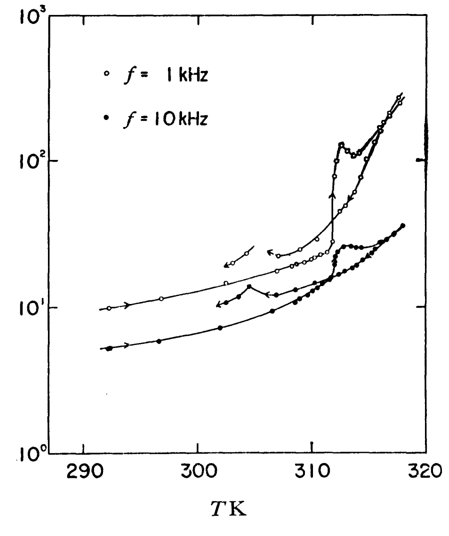

Fig. 2. Dielectric constant ε' at 1 kHz (○) and 10 kHz (●).

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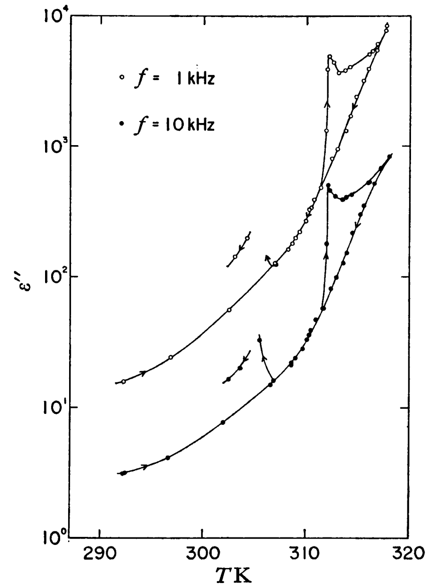


Fig. 3. Dielectric loss factor ε'' at 1 kHz (○) and 10 kHz (●).

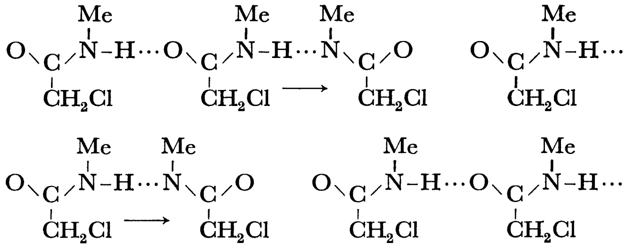
III can exist at room temperature as a metastable phase for a few days but it transforms gradually to Phase II at room temperature, and (4) a sharp transformation of Phase III to Phase II occurs at about 283 K when Phase III is heated from a low temperature with an exothermic phenomenon as shown in the curve f in Fig. 1.

Two ^{35}Cl NQR lines were observed only in Phase II. The resonance frequencies are $\nu_1=34.658\pm0.003$ and $\nu_2=34.783\pm0.001$ MHz at 24.2 K, which decreased monotonously and merged into a single line above 304 K ($\nu_1=\nu_2=33.381$ MHz at 310.2 K). The ^{35}Cl spin-lattice relaxation time T_1 changes slightly from 30 ms at 170 K to 7 ms at 309 K. This fact shows that the internal rotation of molecules is not seen until the transition point T_c is reached. Because the resonance lines are not observable in Phase I, it is considered to be a disordered phase probably with respect to the molecular conformation.

On the other hand, dielectric constant and the loss factor ($\varepsilon'=9.72$, $\varepsilon''=15.9$ at 292 K, $f=1$ kHz) increase gradually with increasing temperature and discontinuous jump occurs at T_c as shown in Figs. 2 and 3.

From ε'' we calculated the DC conductivity σ according to the equation $\sigma=(1/2)\varepsilon''f$. The values of σ (in 10^{-8} ohm^{-1}cm^{-1}) were 0.79 (292 K), 9.4 (309 K), 77 (312 K), and 264 (316 K).

The very high conductivity in Phase I may be interpreted in terms of the proton transfer mediated by the internal rotation of –CONHCH$_3$ group about the C–C bonds as follows:



This mechanism is similar to that proposed for the conduction in imidazole crystal.[5]

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