^{35}Cl NQR in Glassy Crystal of 2-chlorothiophene

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Stable crystalline 2-chlorothiophene has two glass transitions at 164 and 186 K. ^{35}Cl NQR measurements were carried out between 77 and 200 K. Two NQR signals with full widths of about 100 kHz at half maximum were observed in this temperature range. The spin-lattice relaxation times T_1 were measured at the two peak frequencies. The activation energy $\Delta\varepsilon_a$ obtained from the results of the T_1 measurements showed a fairly good agreement with those estimated from calorimetric measurements.

Key words: NQR; 2-chlorothiophene; Glassy Crystal; Glass Transition.

I. Introduction

A glass transition is a freezing phenomenon of a molecular configurational motion. It is observed in the liquid and crystalline state [1]. In the first case the positional and orientational disorder remains, while in the latter case the position of the centers of the molecules remains fixed while their orientation remains disordered. The relaxation phenomena observed near the glass transition temperature in the liquid state are very complicated. The temperature dependence of the relaxation times deviates from the Arrhenius law. The enthalpy relaxation process exhibits non-exponential character and the relaxation function shows a non-linearity to the temperature or pressure jump [2, 3]. The relaxation phenomena in the glassy crystal are simpler. The temperature dependence of the relaxation times follows the Arrhenius law. The enthalpy relaxation process is exponential and the relaxation function is linear with respect to the jump [4 - 9].

2-chlorothiophene, a plane molecule having a triple point of fusion of 201.3 K, has been shown by adiabatic calorimetry to have two glass transitions at 164 and 186 K in the stable crystalline state [4]. In general, the correlation time of the molecular motion falls in the range of 10^{-12}-10^{-16} s at infinite temperature and slows down to about 10^3 s at the glass transition temperature [10]. For reorientational motions of 2-chlorothiophene, which freeze out at the glass transition temperatures, the activation energies can be estimated to be about 50 - 70 kJmol^{-1} under the above assumption. In the present study we attempted to get more detailed information about the molecular motions related to the glass transitions.

II. Experimental

Extra-pure 2-chlorothiophene, purchased from Tokyo Kasei Kogyo Co., Ltd., was first distilled fractionally using a concentric type home-made rectifier, then dehydrated through coexistence with molecular sieve 3A (Wako Pure Chemical Industries, Ltd.) in vacuum for 15 h, and purified by vacuum distillation two times. The purity of the sample was determined to be 0.99983(3) by adiabatic calorimetry [4].

The sample was loaded into a glass tube under a helium gas pressure of 30 kPa. It was put into a cryostat of the NQR spectrometer, which was build in our laboratory. ^{35}Cl NQR signals were observed by use of a spin-echo method. The spin-lattice relaxation time T_1 was measured by use of a π-τ-$\pi/2$-τ_e-π pulse sequence.

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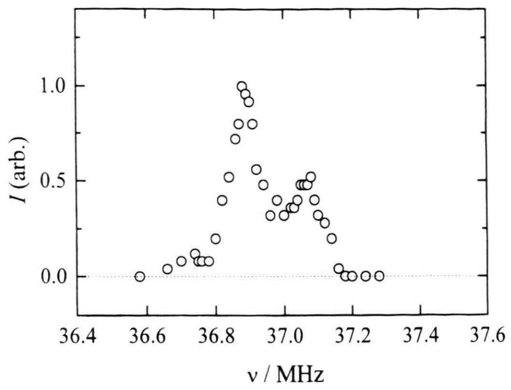

Fig. 1. Frequency dependence of the NQR signal intensity of crystalline 2-chlorothiophene at 77 K.

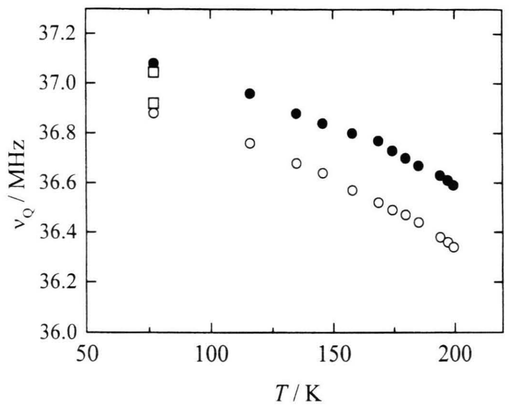

Fig. 2. Temperature dependences of the peak frequencies of the ^{35}Cl NQR spectra. Open squares stand for the data reported in [11].

III. Results and Discussion

The NQR experiments were carried out in the temperature range 77 to 200 K. Figure 1 shows the frequency dependence of the NQR signal intensity at 77 K. Two broad signals, which have a full width of about 100 kHz at half maximum, were observed in the temperature range studied. The resonance frequencies of 36.88 and 37.08 MHz at 77 K are to be compared with the reported values of 36.92 and 37.044 MHz at 77 K by Voronkov *et al.* [11]. The signals could be observed up to just below the triple point of fusion. At 199.5 K the frequencies were determined to be 36.34 and 36.59 MHz. Figure 2 shows the temperature dependence of the two peak frequencies. No anomalies in the temperature dependence of the frequencies at the glass transition points were observed. It has been reported for thiazole that the temperature dependence of the ^{14}N NQR signal intensity shows a bend at the glass transition temperature measured by DSC [12]. In our measurement, however, it is difficult to discuss the temperature dependence of the signal intensity since no reference signal was employed to calibrate the spectrometer sensitivity.

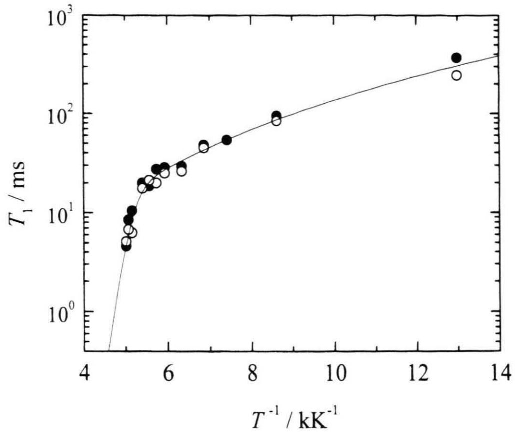

Fig. 3. Temperature dependences of spin-lattice relaxation times T_1 (open and solid circles) at the low- and high-frequency peaks of the ^{35}Cl NQR spectra. The solid curve represents the fitting to the equation, $1/T_1 = aT^n + b \exp(-\Delta\varepsilon_a/RT)$.

Figure 3 shows the temperature dependences of spin-lattice relaxation times T_1 of the two signals. They were almost equal in the whole temperature range studied. The temperature dependence of T_1 can be interpreted by the equation [13]

$$1/T_1 = aT^n + b \exp(-\Delta\varepsilon_a/RT).$$

The least-squares fitting calculations by use of the above equation resulted in $n = 3.1$, $a = 5.1\times10^{-6}\ \mathrm{s}^{-1}\ \mathrm{K}^{-n}$, $b = 1.2\times10^{16}\ \mathrm{s}^{-1}$, and $\Delta\varepsilon_a =$ 53 kJ mol^{-1}. The activation energy $\Delta\varepsilon_a$ obtained from the NQR measurements showed a fairly good agreement with the estimated value from the calorimetric measurements. However, the correlation time at the glass transition temperature of 164 K, estimated from the Arrhenius type part of the temperature dependence of $1/T_1$ is shorter by about three orders of magnitude than the time of 10^3 s which is usually adopted at the glass transition temperature. It is suggested that the relaxation process effective in the NQR experiments is not directly connected to the motion that is frozen at the glass transition temperature, but is a local reorientational motion of molecules. Local means a reorientational motion between local minima in a single potential well corresponding to one of the environments responsible for the glass transitions.

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