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A Kinetic Study on the Response of the Relaxation Time of the α Process to Quick Temperature Change around the Glass Transition

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Glass transition is characterized by the relaxation time of the α process (τ_α) which increases abruptly on cooling towards the glass transition temperature. Temperature dependence of τ_α has been studied extensively.[1)] In experimental studies τ_α is measured after the sample temperature reaches the aimed value and becomes stable. In order to avoid temperature disturbance temperature is controlled slowly. On the other hand in this study sample temperature was changed quickly in order to investigate whether or not τ_α changed with retardation to the temperature change. It seems to be natural to consider that retardation should be observed because the atomic scale structure, on which τ_α is dependent, changes with retardation to the quick temperature change near the glass transition temperature. We carried out experiments to measure the retardation of τ_α and confirmed existence of it. However, it should have been noted that the retardation time of τ_α to the quick temperature change, written as τ_τ below, exhibited temperature dependence notably different from that of τ_α. This result suggested that the origin of τ_τ was different from that of τ_α.

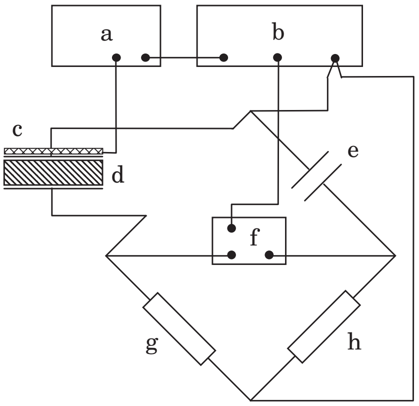

Fig. 1. A schematic diagram of the measurement system. The sample is set in the Wheatstone bridge with a heater for temperature modulation. The system is composed of a: power amplifier, b: function generator, c: heater, d: sample, e: electric capacitor, f: lock-in amplifier, g and h: electric resistance.

The experimental technique is briefly explained below. A new technique called temperature modulated dielectric measurement (TM-dielectric measurement) has been developed in the authors' laboratory. Conventional Wheatstone bridge was utilized to measure the electric capacitance of the sample. In TM-dielectric measurement the sample temperature was modulated sinusoidally with time. A schematic diagram of the experimental system is shown in Fig. 1. According to the temperature modulation the value of τ_α, on which the complex electric capacitance of the sample was dependent, changed sinusoidally at the angular frequency of the temperature modulation, ω_T. This led to nonlinear relationship between the voltage applied to the electric capacitor including the sample and the electric current passing through it. Consequently although the voltage applied to the Wheatstone bridge was purely sinusoidal with the frequency of ω_V, the voltage measured with the lock-in amplifier in Fig. 1 was composed of three Fourier components with the frequencies of ω_V, $\omega_V + \omega_T$ and $\omega_V - \omega_T$ with the first order approximation. The ω_V component was the ordinary linear response. The nonlinear components with the frequencies of $\omega_V + \omega_T$ and $\omega_V - \omega_T$ provided the information about the response of τ_α to the temperature modulation.

The complex amplitude of the measured voltage with the frequency of $\omega_V + \omega_T$ is written as $A_{\Delta+}^*$ below. The nonlinear complex electric capacitance of the sample, C_+^*, is defined by the ratio of the complex amplitude of the $\omega_V + \omega_T$ component of the charge on the electrode to that of the purely sinusoidal voltage with the frequency of ω_V applied to the electrode. The next equation is derived through analysis of the electric circuit of Fig. 1:

$$C_+^* = \frac{A_{\Delta+}^*}{A_V^*} \cdot \frac{(1 + \mathrm{i}(\omega_V + \omega_T)C_0^*(\omega_V)R)(1 + \mathrm{i}\omega_V C_0^*(\omega_V)R)}{\mathrm{i}(\omega_V + \omega_T)R}. \tag{1}$$

Meaning of the symbols are as follows; C_0^*: electric capacitance of the sample measured with the conventional dielectric measurement at the frequency given in the parenthesis, R: electric resistance in the Wheatstone bridge, A_V^*: the complex amplitude of the voltage applied to the Wheatstone bridge. C_+^* can be calculated from the dielectric coefficient of the sample which changes at the frequency of ω_V along with τ_α. Frequency response function, σ_τ^*, of τ_α to the temperature modulation is defined by the next equation.

$$\sigma_\tau^* = -\frac{1}{\overline{\tau_\alpha}} \cdot \frac{A_{\tau\alpha}^*}{A_T^*}, \tag{2}$$

where $\overline{\tau_\alpha}$, $A_{\tau\alpha}^*$, and A_T^* are the value of τ_α without the temperature modulation and the complex amplitudes of the modulated components of τ_α and the temperature, respectively. Therefore an equation connecting C_+^* to σ_τ^* can be deduced. From this equation and eq. (1) next equation is obtained:

$$\sigma_\tau^* = \frac{2\omega_T(1 + \mathrm{i}(\omega_V + \omega_T)C_0^*(\omega_V)R)(1 + \mathrm{i}\omega_V C_0^*(\omega_V)R)}{A_V^* A_T^* \omega_V(\omega_V + \omega_T)R(C_0^*(\omega_V + \omega_T) - C_0^*(\omega_V))} A_{\Delta+}^*. \tag{3}$$

The values of σ_τ^* were calculated from the experimental results using eq. (3).

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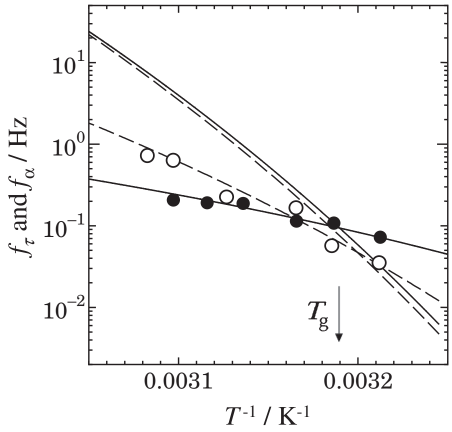

Fig. 2. Temperature dependence of f_τ and f_α. Solid circles with a solid curve are f_τ of the spin coat sample. Open circles with a broken curve are f_τ of the melt press sample. Solid and broken curves without circles are f_α of the spin coat sample and the melt press sample, respectively. The arrow shows the position of T_g on the horizontal axis.

The sample material was atactic poly(vinyl acetate) ($M_w = 260{,}000$, $T_g \sim 40\,°\mathrm{C}$). Two types of the sample were used: a melt press film and a spin coat film with the thickness of 40 µm and 280 nm, respectively. The spin coat sample gives better signal because of the large electric capacitance. However, attention should be paid to artifact due to the molecular orientation in the spin coat sample. The orientation effects can be checked comparing the result from the spin coat sample with that of the melt press sample. The amplitude of the temperature modulation was *ca.* 0.8 K. Measurement was carried out within the frequency range of the temperature modulation from 0.05 to 0.30 Hz. Frequency of the voltage applied to the Wheatstone bridge was 10 Hz. The value of τ_τ was estimated fitting the Cole–Cole type response function to the measured σ^*_τ.

Temperature dependence of $f_\tau = 1/2\pi\tau_\tau$ is shown in Fig. 2 together with $f_\alpha = 1/2\pi\tau_\alpha$ estimated from the linear component of the measured signal. It can be seen that f_τ decreased (τ_τ increased) notably as the temperature decreased. However, temperature dependence of f_τ was much weaker than f_α. At a temperature around T_g the curves of f_τ and f_α crossed each other. These were observed both in the spin coat sample and the melt press sample. This means that these results could not be attributed to the molecular orientation. In both samples the values of τ_τ around T_g were the order of 1 s. These experimental results explain why τ_τ has not been found, although poly(vinyl acetate), known as a model polymer for the dielectric measurement, has been studied in detail by many researchers. The sample temperature can not be stabilized in 1 s. Therefore before the measurement at T_g or higher starts τ_τ already reached the equilibrium value at the temperature. On the other hand at temperatures lower than T_g τ_τ is much shorter than τ_α. It is difficult to detect the effects of τ_τ in such condition. There is volume change induced by the temperature modulation[2] and it leads to the non-linear response as well. Theoretical analysis shows that such non-linear response should exhibit two step change in the temperature dependence at a fixed ω_T and ω_V. However, such behavior has not been observed within the experimental error.

Notable difference between the temperature dependences of τ_τ and τ_α suggested that the former was not the structural relaxation time. It seems that τ_τ is essentially related to the complex dynamics in the glass forming system. Mode coupling theory[3,4] has been extensively studied, but the nature of the four body correlation function included in the theory has not been elucidated experimentally. If τ_τ can be regarded as the correlation time of τ_α it is expected that τ_τ provides information about the four body correlation function. Free energy landscape picture[5] was successfully applied to temperature dependence of material properties such as the specific heat. Free energy landscape characterizes the dynamics of the glass forming system and its temperature dependence. From this viewpoint τ_τ might be regarded as the time necessary to change from a low temperature landscape to high temperature one after a temperature jump. Dynamic heterogeneity visualized in the computer simulation[6] showed that highly mobile molecules form a domain and such domains are distributed in the system. It is considered that τ_τ might be the time required for renewal of the domain size and/or distribution induced by a temperature jump. In any case τ_τ measured with TM-dielectric measurement provides useful information for studies on the dynamics of the glass forming systems.

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