Slow dynamics of supercooled liquid revealed by Rayleigh scattering of Mössbauer radiation method in time domain

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Abstract Characteristic relaxation times τ of the microscopic correlation in o-terphenyl and glycerol were obtained by a time-domain interferometry method using nuclear resonant scattering of synchrotron radiation. From the temperature dependence of τ, a new decoupling temperature 278 K, which is below the conventional decoupling temperature 290 K, was obtained for o-terphenyl. Furthermore, we found a liquid-like relation between τ and q (momentum transfer) as $\tau \propto q^{-2}$ at 285 K in o-terphenyl and 260 and 265 K in glycerol. However, an anomalous q dependence of the slow β relaxation time, $\tau \propto q^{-2.9}$ and $q^{-3.8}$, was observed in deeply supercooled (265 K) and glass (240 K) states, respectively, in o-terphenyl, indicating specially restricted dynamics of the slow β process.

Keywords Nuclear resonant scattering · Time-domain interferometry method · Slow dynamics · Supercooled liquid

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1 Introduction

The molecular dynamics in glass forming liquids and polymers under supercooled liquid state has been studied so much to understand the nature of the glass transition [1, 2]. In particular, the relaxation process known as the α process, which is diffusion process, has been considered to be closely related to the glass transition. On the other hand, a process called the slow β (Johari-Goldstein) process seems to branch from the α process with cooling and can be observed also in glass state, but its nature has not been fully understood. However, the slow β process seems to be also a key to reveal the microscopic dynamical picture in supercooled liquid close to the glass transition temperature T_g because the branching phenomenon is observed in many glass formers [3]. Moreover, the decoupling has been considered to occur around the temperature of the change of the α-relaxation dynamics [3]. In addition to the slow β process itself, the microscopic picture of this decoupling phenomena has not been clarified sufficiently. It is partly due to the difficulty to obtain the microscopic information on the decoupling phenomenon by the conventional methods such as a dielectric relaxation method, which has limited information on the length scale of the relaxation. On the other hand, the decoupling of the slow β process from the α process in polymer, for example, has been studied with the assignment of the length scales of relaxation processes by selecting a momentum transfer q using a neutron spin echo (NSE) method [4–6], and their results were discussed with simulation results [7]. In their studies, the slow β process was discussed with the hopping model, and the average jump distance was estimated. Moreover, the degree of the heterogeneous dynamical behavior was discussed by considering q dependence of the relaxation time τ of the α process and the stretching parameter β_{KWW} of the Kohlrausch-Williams-Watts (KWW) function [8]. Therefore, the NSE method is thought to be an effective method for the study on microscopic dynamics. However, due to the limitation of the accessible q and time range, the decoupling behavior of the slow β process from the α process and the detailed q dependence of τ at low temperatures close to T_g have not been fully examined.

A Rayleigh scattering of Mössbauer radiation (RSMR) method using a radioactive isotope (RI) has also been used to study the microscopic slow dynamics [9]. In this method, a gamma ray from the first excited state of ^{57}Fe nuclei, which has an energy of 14.4 keV (the momentum is 73 nm^{-1}) with the natural energy width of 4.67 neV is frequently used as a probe for a quasi-elastic scattering measurement at a large q region such as the order of 10 nm^{-1}. However, detailed studies such as the study on the q dependence of τ requires much measuring time because the gamma rays from RI sources are emitted equally in all direction and directional probe gamma rays, which are required for the measurement, are scarcely available. A time-domain interferometry (TDI) method using synchrotron radiation is a time-domain analogue of the RSMR method [10–16]. Owing to the directionality characteristic of SR, the TDI method enables more efficient measurement. The relaxations of the density correlation are reflected on the time spectrum of coherent nuclear resonant scattering as a disappearance of the quantum beat pattern, and the disappearance gives the intermediate scattering function $F(\boldsymbol{q},t)$. Using the TDI method, we studied the microscopic dynamic behavior of a typical glass-forming molecule o-terphenyl, which has been studied intensively because the molecular shape of o-terphenyl is simple and favorable for the model system of fragile glass formers [17]. Neutron quasi-elastic scattering experiments on o-terphenyl have been performed above 290 K [18–20], which has been known to be the crossover temperature of the dynamics and the decoupling temperature of the α and slow β processes [21, 22]. However, microscopic dynamical behavior around the temperature has been still unclear. These days, new experimental results on the slow microscopic dynamical
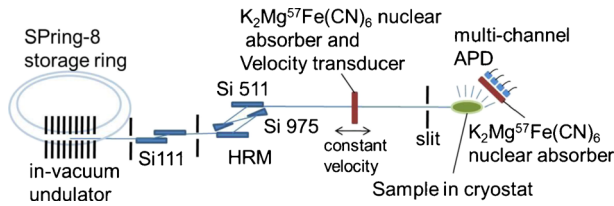
Fig. 1 Experimental setup of TDI method at BL09XU in SPring-8. See main text for detailed information

behavior in o-terphenyl obtained by the TDI method was reported [23]. In this paper, we show further TDI results on o-terphenyl as well as results on glycerol, which give additional information on the previous result.

2 Experiment

The experiments were performed at the NRS beamline (BL09XU) of SPring-8 in Japan. The experimental setup of TDI is shown in Fig. 1. An incident radiation of 3.5-meV energy width at the excitation energy of the 1st nuclear excited state of ^{57}Fe was obtained using a high-resolution monochromator (HRM) consisting of asymmetric Si (5 1 1) and Si (9 7 5) channel-cut crystals. The storage ring was operated in a several-bunch timing mode (1/7-filling + 5-bunch mode, with a bunch interval of 684.3 ns in the several 5 bunches) during our experiments on both o-terphenyl and glycerol. The temperature of the sample was controlled by a He-flow cryostat. A multielement Si-avalanche photodiode (APD) detector was used for counting gamma rays (nuclear resonant scattering). The nuclear absorbers were $K_2Mg^{57}Fe(CN)_6$, whose ^{57}Fe density is 1.0 mg/cm^2. The $K_2Mg^{57}Fe(CN)_6$ absorber before the sample was driven with a velocity of around 15 mm/s by using a velocity transducer. O-terphenyl was produced by Tokyo Chemical Industry Co., Ltd., whose T_g was measured at 244 K using differential scanning calorimetry (DSC). The temperature dependence of TDI time spectra was measured between 240 and 300 K at q-values of 14 and 23 nm^{-1}, which are the first peak and valley of $S(q)$, respectively. The melting point of o-terphenyl is around 330 K. The sample, which was under supercooled liquid state more than one week at room temperature ($\sim$300 K), was used. The cooling rate of the sample is the order of 0.1 K/s. It was confirmed that the temperature history (such as a direct cooling from the room temperature, much slower cooling, and heating from the glass state) of the sample doesn't affect the result within our experimental accuracy.

The q dependence of the TDI time spectra of o-terphenyl was observed at 240, 265, and 285 K at q-values between 14 to 48 nm^{-1}. Also glycerol, which is spectroscopic graded and purchased by Sigma-Aldrich, has been studied at 260 and 265 K at q-values between 20 and 41 nm^{-1} to support the result of o-terphenyl. Examples of the obtained TDI time spectra are shown in Fig. 2. These least square fittings were performed by using the theoretical equations available elsewhere [11, 12]. The KWW function was used for $F(\boldsymbol{q},t)$ with fixed β_{KWW} value of 0.6 for o-terphenyl [19, 23] and 0.8 for glycerol [24]. From the obtained τ, a mean relaxation time $\langle \tau \rangle$, which factors in the stretched exponential decay, is calculated according to $\langle \tau \rangle = \tau \Gamma(1/\beta_{\text{KWW}})/\beta_{\text{KWW}}$ [17] where Γ is the gamma function.
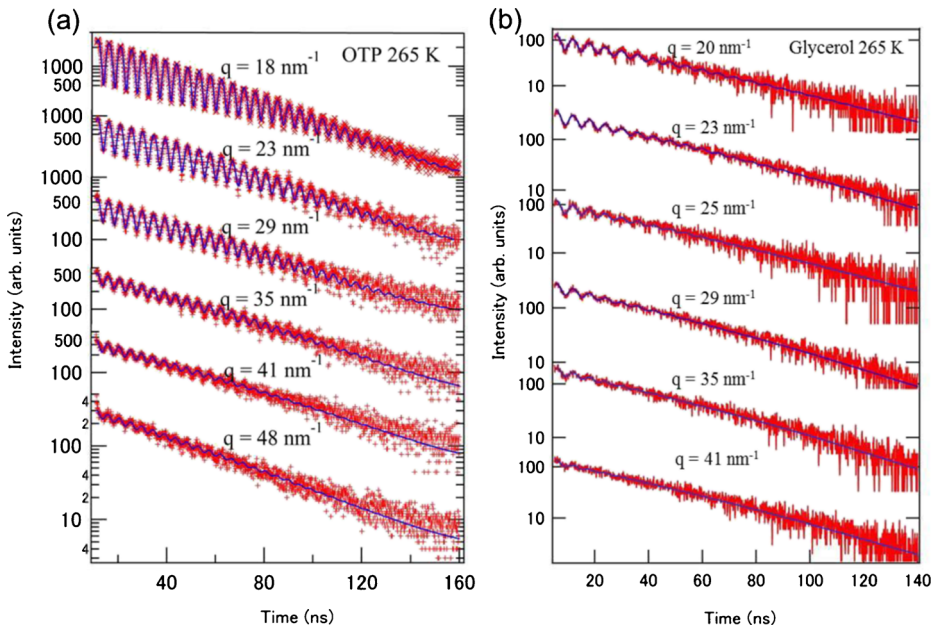
Fig. 2 Examples of TDI time spectra and their fitting curves at several q at 265 K for **a** o-terphenyl (OTP) and **b** glycerol

3 Results and discussion

In the case where the q value is 14 nm^{-1} in o-terphenyl, the T dependence of $\langle\tau\rangle$ obeys the Vogel-Fulcher-Tammann (VFT) law $\langle\tau(T)\rangle \propto \exp\{DT_0/(T - T_0)\}$ as shown in Fig. 3, where T_0 is the Vogel-Fulcher temperature and D is the fragility index [1, 2]. The parameters [$D = 3.1(3)$, $T_0 = 235(26)$ K] and the time scale of $\langle\tau\rangle$ are consistent with those of the reported values for the α process [3, 22, 25]. This result indicates that the relaxation observed at q-value of 14 nm^{-1} is due to the α process. Since the corresponding first peak position of $S(q)$ reflects the inter-molecular correlation, it is confirmed that this structural relaxation process is the α process. On the other hand, for the q value of 23 nm^{-1}, the character of T dependence of $\langle\tau\rangle$ was found to change at the temperature 278 K as shown in Fig. 3. The T dependence of $\langle\tau\rangle$ obeys the VFT law above 278 K but the Arrhenius law $\langle\tau(T)\rangle \propto \exp\{E/T\}$ below 278 K. The obtained activation energy E is 36 (9) kJ/mol and is consistent with those of the slow β process obtained by the dielectric method [21, 26, 27]. Therefore, the relaxations observed at q-value of 23 nm^{-1} below 278 K are concluded to be due to the slow β process. Since the behavior of the T dependence of $\langle\tau\rangle$ above 278 K at q-value of 23 nm^{-1} is similar to that for the q value of 14 nm^{-1}, the relaxation observed at $q = 23$ nm^{-1} above 278 K is due to the α process. The relaxation time of the α process below $T_{\alpha\beta}$ expected from the extrapolation of the relaxation time above $T_{\alpha\beta}$ is likely to be much longer than that of the slow β process as shown in Fig. 3 even if it exists and the obtained E value is consistent with those obtained previously [18, 26, 27] as discussed above. Therefore, the contribution to the T-dependence of $\langle\tau\rangle$ (23 nm^{-1}) of the α process well below $T_{\alpha\beta}$ is expected to be negligible. Consequently, the turning temperature of 278 K is interpreted to be the decoupling temperature $T_{\alpha\beta}$ at which the main origin of
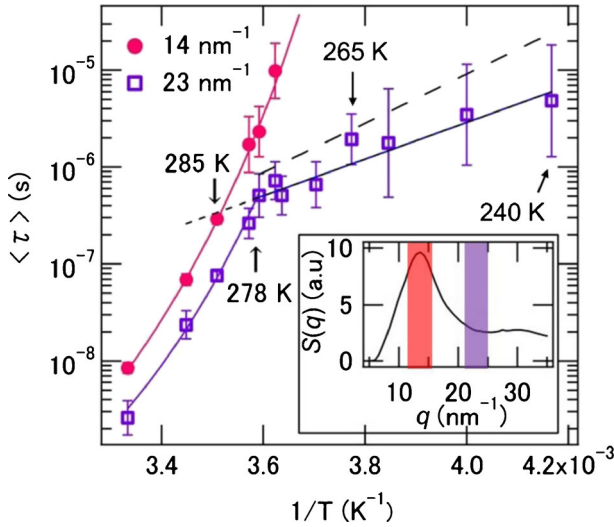
Fig. 3 *T* Dependence of $\langle\tau\rangle$ at $q = 14$ and 23 nm^{-1} in *o*-terphenyl. The *solid lines* show the fitting curves as discussed in the main text. *Short* and *long dashed lines* show the extrapolation of Arrhenius fitting curve and dielectric relaxation time of the slow β process, respectively [27]. Inset shows $S(q)$ and q regions used for the $\langle\tau\rangle$ measurement

the relaxation process observed at $q = 23$ nm^{-1} changes from the α process to the slow β process with cooling. The temperature $T_{\alpha\beta} \sim 278$K is lower than 290 K which has been believed to be the decoupling temperature so far [3].

Here, it's worth to note the difference between dielectric and TDI-relaxation times. The α and slow β processes are considered to occur at several length-correlation scales. The dielectric method provides the α- and slow β-relaxation times, which are total relaxation times of all involved length scales, respectively. Instead, the TDI method can measure the relaxation time of a specific length scale. Our experiment indicates that the inter-molecular correlation obtained at $q = 14$ nm^{-1} relaxes with the dielectric relaxation time of the α process [3, 22, 25], and the obtained $\langle\tau\rangle$ at $q = 23$ nm^{-1} and below $T_{\alpha\beta}$ is similar to the dielectric relaxation time of the slow β process [21, 26, 27]. Actually, as shown in Fig. 3, we found that the crossover point of the extrapolation of the Arrhenius law obtained at 23 nm^{-1} and the VFT law obtained at 14 nm^{-1} is around 285 K, which is close to the conventional temperature 290 K.

The α-relaxation time obtained at $q = 23$ nm^{-1} and above $T_{\alpha\beta}$ is faster than that at $q = 14$ nm^{-1} because the local correlation (with smaller length scale than the inter-molecular scale) observed at $q = 23$ nm^{-1} relaxes faster than inter-molecular correlation by the α process. Usually, $T_{\alpha\beta}$ has been decided as the crossing point of the extrapolation of the dielectric slow β-relaxation times and the dielectric α-relaxation times because these dielectric relaxation times could not be observed separately around $T_{\alpha\beta}$. However, our experimental study clearly revealed that the extrapolation itself doesn't have a physical meaning because the α and slow β processes occur at different length scales. Moreover, it is shown from our experiment the slow β-relaxation time splits from the relaxation time of the local correlation originating from the α process, which is faster than the dielectric relaxation time of the α process. As mentioned above, $T = 290$ K is known also as the crossover temperature, at which the α-relaxation dynamics starts to change. Therefore, our
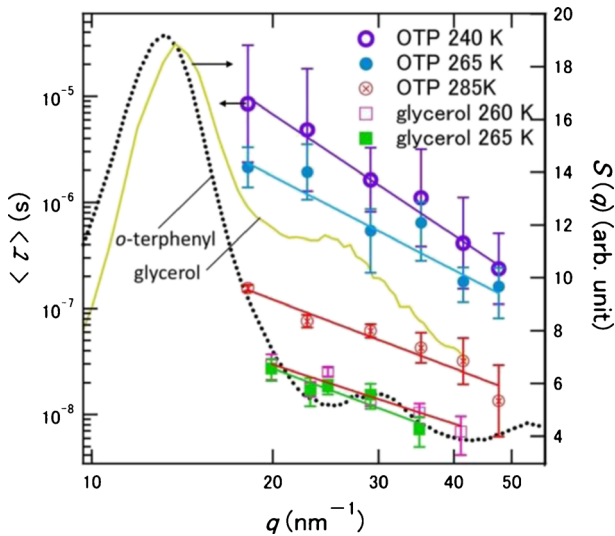
Fig. 4 q Dependence of $\langle \tau \rangle$ at $T = 240$, 265 and 285 K and static structure factor of o-terphenyl (OTP), which is shown as *dashed line*. Also, q dependence of $\langle \tau \rangle$ at $T = 260$ and 265 K and the static structure factor of glycerol (red solid line) are shown. *Solid straight lines* show these fitting curves of $\langle \tau \rangle$

result indicates that further cooling from the crossover temperature seems to be required to decouple the slow β process from the α process [28].

Now, to reveal the detailed property of the slow β process, we measured the q dependence of the $\langle \tau \rangle$ at 265 K below $T_{\alpha\beta}$ at the q region, where the contribution of the slow β process is dominant (shown in Fig. 4). It is known that in both the self and mutual correlation functions, the q dependence of $\langle \tau \rangle$ in liquids follows $\langle \tau \rangle \propto q^{-2}$ indicating that molecules diffuse relatively freely. This relation was confirmed for o-terphenyl at T above 290 K [18, 19, 29]. However, towards glass transition, the dynamical behavior of the molecules is expected to change from liquid-like to glass-like. Actually, this result of o-terphenyl at $T = 265$ K indicates that $\langle \tau \rangle$ obtained at 48 nm^{-1} is about two times shorter than the value expected by the relation $\langle \tau \rangle \propto q^{-2}$ using the $\langle \tau \rangle$ obtained at 18 nm^{-1}. To elucidate the anomalous dynamical behavior at $T = 265$ K, q dependence of $\langle \tau \rangle$ was investigated by fitting with the power law $\langle \tau \rangle \propto q^{-n}$, where n is a power law index. As shown in Fig. 4 fits at several temperatures were performed in the region $18 \leq q \leq 48$ nm^{-1}, in which the effect of de Gennes narrowing can be neglected [19]. At $T = 265$ K a value of $n = 2.9(5)$ is obtained. By obtaining q dependence of $\langle \tau \rangle$ at 240 K, we also found further anomalous dynamical behavior with $n = 3.8 (7)$. Instead, we obtained the liquid-like q-dependence with $n = 2.2(2)$ at 285 K, which is close to the crossover temperature. Using the power law index, the dependence of the mean squared displacements on time is expressed as $\langle \Delta r^2(t) \rangle \propto t^{2/n}$ for the case of the translational diffusion [8], where $\Delta r(t)$ is the displacement of a molecular position within t. For temperatures where $n > 2$, the mean squared displacement becomes sub-linear in time indicating the restricted molecular motions. Thus, $n = 2.9(5)$ at 265 K and $n = 3.8(7)$ at 240 K indicate a molecular diffusion begins to be restricted around 290 K and is the characteristic of the microscopic dynamical behavior. On the other hand, the origin of the slow β process has been proposed to be the rotation of the phenyl ring for the case of o-terphenyl [30]. Moreover, a small rearengement of the whole molecule, which was assigned to be an origin of the slow β process in similar

small molecule liquid, may also contribute to the slow β process in *o*-terphenyl [31]. Both motions can cause a relaxaton of the intra-molecular correlation. Therefore, both of the interpretations are consistent to our experimental result. Our result of the mean squared displacement sub-linear in time is similar to the mean squared displacement obtained in concentrated colloidal system [32]. This restricted dynamical behavior of the slow β process is also consistent with the results from a NMR measurement [33]. For the case of glycerol, we found the q-dependence of $\langle \tau \rangle$ with $n = 1.9(4)$ and $2.1(6)$ at 260 and 265 K, respectively. Here, the T_g and the crossover temperature of glycerol are $\sim$190 K and around $225 \sim 259$ K, respectively [34]. Therefore, we found the q dependence of $\langle \tau \rangle$ follows $\langle T \rangle \propto q^{-2}$ at T above the crossover temperature indicating liquid-like diffusion also for glycerol. Further study is in progress to know the universal restricted character of microscopic relaxation in deeply supercooled liquids.

4 Conclusions

We have found the decoupling temperature of *o*-terphenyl to be 278 K, which is clearly below the previously determined decoupling temperature 290 K. This difference is due to the fact that the slow β process is a local process and doesn't split from the α process of structural relaxation. This result indicates further cooling from the temperature 290 K, at which the α-relaxation dynamics changes, is required to decouple the slow β process from the α process. Moreover, by observing q dependence of $\langle \tau \rangle$ at the q and T range closely relating to the slow β process, we found anomalous q dependence of $\langle \tau \rangle$ in both supercooled and glass states of *o*-terphenyl indicating a restricted dynamics of the slow β relaxation.

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