

Slow dynamics of supercooled liquid *o*-terphenyl

The molecular dynamics in glass-forming liquids and polymers toward glass transition has been studied to understand the nature of glass transition. Relaxation process known as the α process, which is the structural relaxation process induced by molecular diffusion, has been thought to be closely related to glass transition. On the other hand, another relaxation process called the slow β (Johari-Goldstein) process, which seems to branch from the α process with cooling and is thought to play an important role in supercooled liquids approaching to the glass transition, has not been fully understood. So far, the decoupling of the slow β process from the α process has been considered to occur at around the temperature at which the properties of the α -relaxation dynamics change. To understand the decoupling phenomenon, the typical glass-forming molecule *o*-terphenyl has been studied [1] by quasi-elastic scattering measurement known as time-domain interferometry

(TDI) using the ^{57}Fe -nuclear resonant scattering (NRS) of synchrotron radiation [2], which is a time-domain analogue of the Rayleigh scattering Mössbauer radiation method [3]. In this method, the beating pattern induced by the interference of the probe and reference NRS is detected in the time domain (examples of the spectra are shown in Fig. 1). The relaxations of the density correlation in the sample are reflected as a disappearance of the beating pattern, which gives the intermediate scattering function; we have assumed the stretched exponential decay function as the intermediate scattering function. The temperature T and momentum transfer q dependences of the mean relaxation times $\langle\tau\rangle$ obtained by the least square fitting of the measured spectra using the function are shown in Fig. 2 and Fig. 3, respectively.

When $q = 14 \text{ nm}^{-1}$, the T dependence of $\langle\tau\rangle$ was observed to obey the Vogel-Fulcher-Tammann (VFT) law with a diverging behavior toward a certain

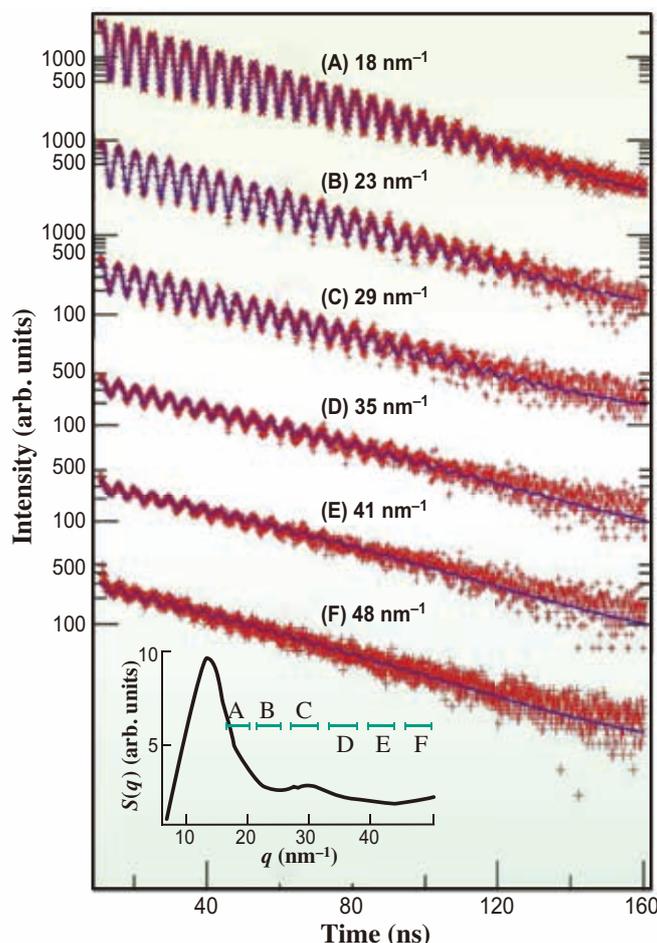


Fig. 1. Examples of TDI time spectra and their fitting curves at various momentum transfers at 265 K. The inset shows the static structure factor and momentum transfer regions used to obtain time spectra.

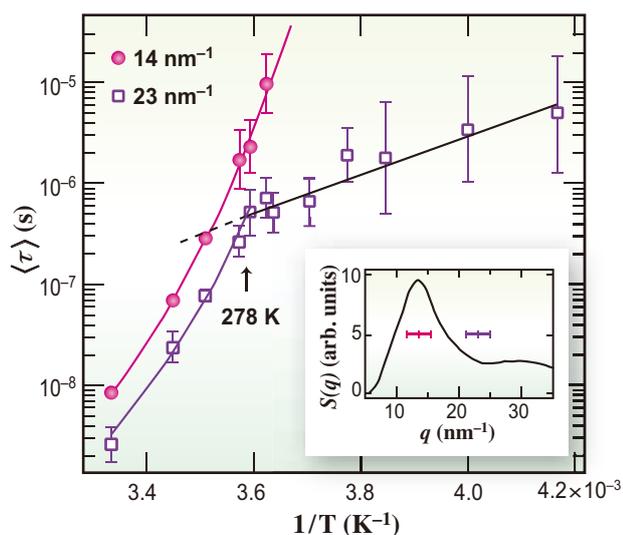


Fig. 2. Temperature dependences of relaxation times at 14 and 23 nm⁻¹. Solid lines indicate the fitting curves of data (see main text). The inset shows the momentum transfer regions used to obtain relaxation times.

temperature near the glass transition temperature, as shown in Fig. 2. Since the diverging behavior is consistent with that reported for the α process and is observed at the peak position of the static structure factor, the relaxation observed at $q = 14 \text{ nm}^{-1}$ is the structural relaxation due to the α process. On the other hand, at $q = 23 \text{ nm}^{-1}$, the character of the T dependence of $\langle \tau \rangle$ was found to change at 278 K. The T dependence of $\langle \tau \rangle$ obeys the VFT law above 278 K, but obeys the Arrhenius law below 278 K. The activation energy of 36 (9) kJ/mol obtained by least square fitting below 278 K is consistent with those of the slow process obtained by the dielectric method. Therefore, the relaxations observed at $q = 23 \text{ nm}^{-1}$ below 278 K are mainly due to the slow β process and occur at the local length scale in *o*-terphenyl. Since the behavior of the T dependence of $\langle \tau \rangle$ above 278 K at $q = 23 \text{ nm}^{-1}$ is similar to that at $q = 14 \text{ nm}^{-1}$, the relaxation observed at $q = 23 \text{ nm}^{-1}$ above 278 K is mainly due to the α process. Therefore, the turning temperature of 278 K is interpreted to be the decoupling temperature $T_{\alpha\beta}$ at which the primary source of the relaxation process observed at $q = 23 \text{ nm}^{-1}$ changes from the α process to the slow β process with cooling. From this result, it can be concluded that the slow β -relaxation process decouples from the relaxation process of the local length scale originating in the α process, which is faster than the mean relaxation of the α process. Owing to the difference in the length scale between the α and the slow β processes, the lines representing these two averaged relaxation times are concluded not to cross in the temperature dependence of the relaxation time as an extrapolation assumed so far.

Since the obtained decoupling temperature is also lower than the changing temperature of the diffusion behavior (290 K) obtained so far, our result indicates that a sufficient solid-like condition achieved by further cooling from 290 K is required for the decoupling of the slow β process from the α process.

Moreover, by measuring the q dependence of $\langle \tau \rangle$ at 265 K (below $T_{\alpha\beta}$) and at q values above the peak of the static structure factor, at which the spatial correlation relaxes mainly by the slow β process, we could obtain an anomalous q dependent behavior of $\langle \tau \rangle$ following the power law $\langle \tau \rangle \propto q^{-n}$ with an n value of 2.9 (5), as shown in Fig. 3. The obtained n value greater than 2 indicates the restricted microscopic dynamical behavior of the slow β process, which is independent of origin. Therefore, we found evidence of the restricted dynamical behavior of the slow β process as an anomalous q dependence of the relaxation time.

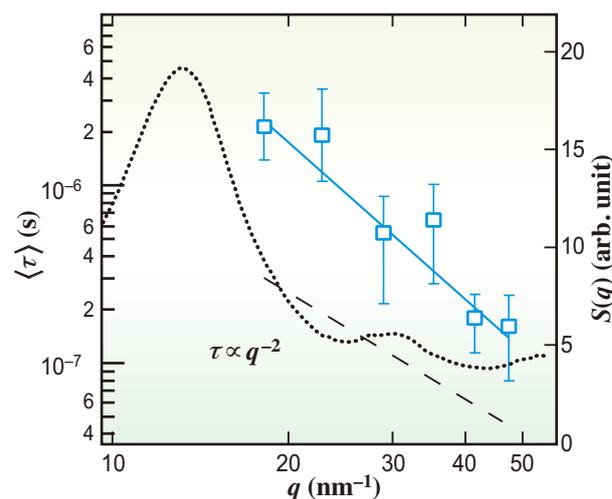


Fig. 3. Momentum transfer dependence of relaxation time at 265 K in higher momentum transfer region than the first peak of the static structure factor. Dot, bold, and dashed lines indicate static structure factor, fitting curve (see main text), and behavior $\langle \tau \rangle \propto q^{-2}$, respectively.

Makina Saito and Makoto Seto*

Research Reactor Institute, Kyoto University

*Email: seto@rri.kyoto-u.ac.jp

References

- [1] M. Saito, S. Kitao, Y. Kobayashi, M. Kurokuzu, Y. Yoda and M. Seto: *Phys. Rev. Lett.* **109** (2012) 115705.
- [2] A.Q.R. Baron *et al.*: *Phys. Rev. Lett.* **79** (1997) 2823.
- [3] D.C. Champeney and F.W.D. Woodhams: *J. Phys. B.* **1** (1968) 620 and references therein.