（ ※本報告書は英語で記述してください。ただし、産業利用課題として採択されている方は日本語で記述していただいても結構です。 ）

CROSS TOKAI Experimental Report J-PARC	承認日Date of Approval 2014/5/22 承認者Approver Kaoru Shibata 提出日Date of Report 2014/5/22
課題番号 Project No. 2013A0093 実験課題名 Title of experiment Dynamic heterogeneity and anomalous glass transition of ultra-thin polymer films 実験責任者名 Name of principal investigator Toshiji Kanaya 所属 Affiliation Institute for Chemical Research, Kyoto University	装置責任者 Name of responsible person Kaoru Shibata 装置名 Name of Instrument/(BL No.) DNA/BL-02 実施日 Date of Experiment 2013/5/17～2013/5/23

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

Hydrogenated polystyrene thin films supported on Al foils

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

It is well known that physical properties of polymer thin films are quite different from those of bulk state. Among them glass transition behavior in polymer thin film is one of the most attractive phenomena. As for polystyrene (PS) thin film a reduction of glass transition temperature (T_g) with film thickness was reported by so many researchers. At present it is considered that such a decrease of T_g with film thickness is mainly attributed to an existence of mobile layer at the free surface, which was directly confirmed by scanning probe microscope. On the other hand glass transition phenomenon in itself is not a thermodynamic transition but relaxation process, hence it is strongly suggested that direct dynamical measurements on polymer thin film is effective for understanding the puzzling mechanism of glass transition in polymer thin films. So far dynamical studies on polymer thin films have not been performed extensively due to experimental difficulties. In order to overcome such a situation we then tried to perform quasielastic neutron scattering (QENS) measurements on polymer thin films.

PS with molecular weight of 2.9×10^5 and molecular weight distribution 1.06 were used for present QENS measurements. PS thin films were prepared by spin-coating toluene solutions on flat glass plates and thin films were removed from glass plates to water surface. Subsequently thin films were collected on Al foil with the thickness of 15 μm. Prior to QENS measurements thin films were annealed at the temperature above bulk T_g to promote structural relaxation. QENS measurements were performed

2. 実験方法及び結果（つづき） Experimental method and results (continued)

With the DNA spectrometer with energy resolutions of about 3 μeV and about 13 μeV at J-PARC. For the evaluation of T_g from QENS measurements we mainly performed elastic window scan from 10K to 413K, which was above bulk T_g.

Figure 1 indicates the temperature dependence of mean square displacement ($\langle u^2 \rangle$), which was evaluated from Q^2 dependence of elastic scattering intensity ($I(Q)$) observed for PS thin films 40 nm thickness. With increasing temperature an increase of $\langle u^2 \rangle$ was seen and further increase of $\langle u^2 \rangle$ was observed at round 400K for both energy resolution. It implies an onset of anharmoic motion or relaxation process. As for bulk sample it was reported that such an onset temperature was coincided with T_g evaluated from DSC or other methods within experimental error [1]. We then try to regard this onset temperature as T_g from QENS measurements and such evaluated T_g s are shown by solid arrows in Figure 1. Interestingly an increase of T_g compared to bulk T_g, which is shown by a dotted line in Figure 1 is clearly observed regardless of energy resolutions. Contrary to our expectation a decrease of mobility was found from present QENS measurements. More interestingly T_g of polymer thin film 40 nm thick seems to be slightly dependent on energy resolution within the limited energy resolution range. In order to verify this quite interesting tendency in more detail we investigated energy resolution dependence of T_g for bulk PS and PS thin film 40 thick including former QENS results, as shown in Figure 2 [2]. As a result T_g from bulk PS is not dependent on energy resolution within the present energy resolution, on the other hand T_g from PS thin film 40 nm thick tends to increase with lowering energy resolution. Hence it is expected that temperature dependence of relaxation time of the α process, which is responsible for glass transition might be dependent on film thickness. In order to prove such an idea we are now performing dielectric relaxation spectroscopy on PS thin film. Furthermore with the combination of the results from present QENS work and dielectric relaxation spectroscopy we try to understand an origin for an increase of T_g with decreasing film thickness and we also try to construct the physical picture for interpreting both the present result and formerly reported ones without inconsistency.

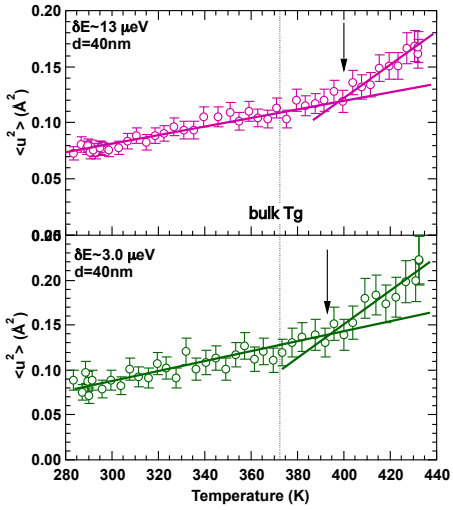

Figure 1 Temperature dependence of $\langle u^2 \rangle$ observed for PS thin films 40 nm thick.

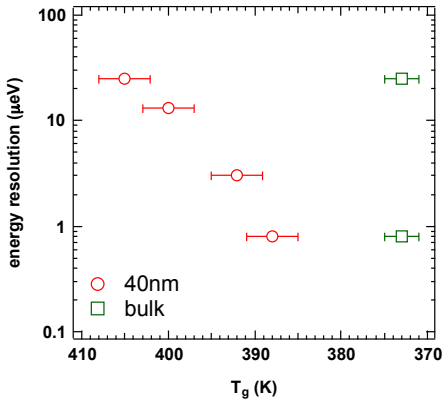

Figure 2 Energy resolution dependence of T_g observed for PS thin films 40 nm thick and bulk PS.

References

[1] T. Kanaya et al., Adv. Polym. Sci. 154, 87 (2001).

[2] R. Inoue et al., Phys. Rev. E 80, 031802 (2009).