MLF Experimental Report

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実験課題名 Title of experiment
Dynamic anisotropy of polymer thin films studied by inelastic neutron scattering

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装置名 Name of Instrument/(BL No.)
BL-14

実施日 Date of Experiment
2012/3/15～3/22

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 (-(C8H8)n-) with the thickness of 1000Å
Hydrogenated polystyrene (-(C8H8)n-) with the thickness of 200Å

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.

Experimental section

We studied the dynamic anisotropy of hydrogenated polystyrene (h-PS) thin films especially focusing on glassy dynamics including low energy excitation (Boson peak) and local relaxation process (fast process) by AMATERAS. For the anisotropy studies, we have to set the scattering vector to both parallel and perpendicular directions of the surface of polymer thin films. First we stack 300 polymer thin films supported onto Al foil plate and such stacked polymer thin films was set at ±45° to the incident neutron beam to realize exact parallel and perpendicular geometries at 2theta=90° for the elastic scattering like Figure 1. In spite of focusing on incoherent scattering from the sample the scattering intensity from polymer thin films are extremely weak, hence we selected the incident neutron energy as 15.0 meV at which the highest neutron flux was obtainable. With this neutron incident energy the exact parallel and perpendicular geometries are hold at Q=3.8 Å^{-1} for the elastic scattering. We measured three different temperature 45, 85K and 300K. The lowest temperature was used for the determination of resolution

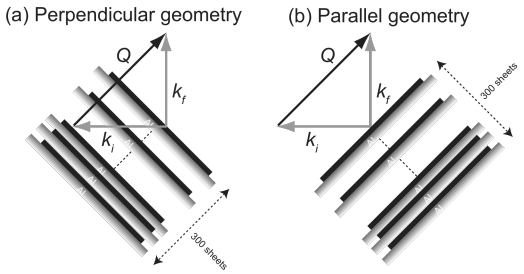

Figure 1. Sample geometries for measurements. (a) Perpendicular and (b) Parallel geometeries. The figures correspond to the case of elastic scattering.

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

function and the measurements at 85K and 300K was used for the observation of Boson peak and fast process, respectively.

Results and discussion

Figure 2 indicates the observed dynamic scattering law $S(Q, \omega)$, which was normalized at elastic peak position observed for 1000 Å and 200 Å PS thin films at Q=3.8 Å^{-1} at reflection (perpendicular) and transmission (parallel) geometries at 300K. Even from PS 200Å thin films we could observe the clear quasielastic scattering, supporting the high quality of data. With decreasing film thickness the quasielastic scattering intensity decreased, it implies the reduction of mobility with film thickness and this observation is consistent with our former works [1]. As for 1000Å thin films, the observed $S(Q, \omega)$ from two geometries (reflection and transmission) coincided, indicating that no dynamical anisotropy was observed for 1000Å thin films. On the other hand, the observed $S(Q, \omega)$ from reflection geometry is slightly higher than that from transmission geometry for 200Å thin films, indicating the observation of dynamical anisotropy in glassy state.

In order to analyze the obtained spectra in more detail, we performed curve fits to the observed $S(Q, \omega)$. At first we tried to fit the observed spectra with a model function given by the sum of a δ-function and a single Lorentzian (model 1), which was used to describe fast process. However we observed a severe discrepancy between the observed spectra and the calculated one due to the existence of broad quasielastic-like component. Normally such broad component can be described by the flat inelastic background, however the flat background seems not be appropriate for the description of broad quasielastic-like component. Hence we tried to fit the spectrum with a model function given by the sum of a delta-function and two Lorentzians (model 2). An example of model fit with model 2 is shown in Figure 3 for 1000Å thin films in refelction geometry and we found that the quality of fit with model 2 was fairy well within the energy range examined. We also tested model 2 for 1000Å in transmission geometry and 200Å thin films in both geometries and we again observed the excellent quality of fit with model 2. At present stage we have not tried the other model, however we would like to adopt model 2 as an initial step. Referring to the former works [1, 2], the relaxation rate (Γ) from the narrow Lorentzian component is consistent with Γ from fast process. Therefore, we would like to discuss the thickness dependence of Γ and fraction from narrow Lorentzian component or fast process in both reflection and transmission geometries (Figure 4). As we have mentioned, no dynamical anisotropy was observed for 1000 Å PS thin films within experimental error. As for 200 Å PS thin films, no change of fraction was observed, however the difference was observable from the relaxation rate of fast process. That is to say, the dynamics in reflection geometry (perpendicular geometry) is more mobile than that in transmission geometry (parallel geometry), indicating that the in-plane motion was more restricted or hindered than out-of-plane motion due to the contribution from substrate. In order to reinforce our results, the spectroscopic studies on PS thin films in glassy state are on progress.

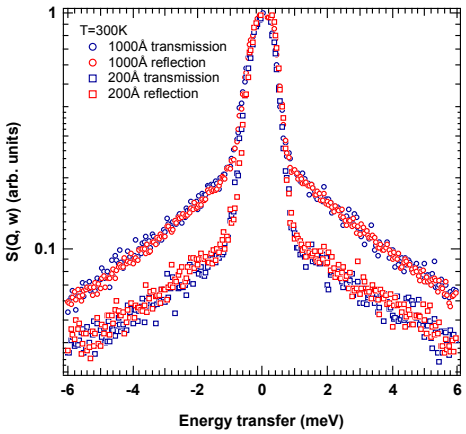

Figure 2. Dynamics scattering law $S(Q, \omega)$ of 1000Å and 200 Å PS thin films at T=300 K measured at Q=3.8 Å^{-1} in both transmission and reflection geometries.

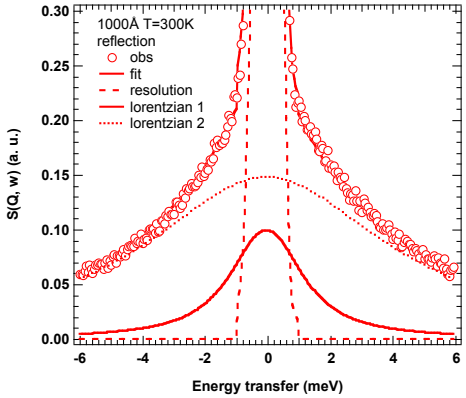

Figure 3. Result of curve fitting with model 2 for 1000 Å PS thin films in reflection geometry at T=300 K.

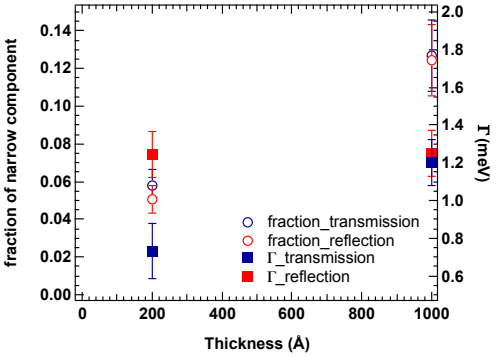

Figure 4. Thickness dependence of fraction and relaxation rate from narrow Lorentian component.

References

[1] R. Inoue et al., Phys. Rev. E, 74, 021801(2006). [2] T. Kanaya et al., J. Chem. Phys. 104, 3841 (1996).