（ ※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 2013/9/18 承認者 Approver Kaoru Shibata 提出日 Date of Report 2013/6/22
課題番号 Project No. 2012B0047 実験課題名 Title of experiment Correlation between gas permeability and local dynamics of poly(4-methyl-1-pentene) 実験責任者名 Name of principal investigator Rintaro Inoue 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.) BL02 実施日 Date of Experiment 2013/3/19～2013/3/26

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 poly(4-methyl-1-pentene) (-(C6H12)n-) (P4MP1)
Hydrogenated poly(3-methyl-1-pentene) (-(C6H12)n-) (P3MP1)

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

P4MP1 of which chemical structure is shown in Fig. 1 exhibited high gas permeability despite of noticeable chemical structure. We considered that dynamical studies on P4MP1 is desirable for understanding the physical origin of high gas permeability of P4MP1, hence we performed quasielastic neutron scattering (QENS) measurements on P4MP1 with DNA. As an initial step, we performed elastic window scan from lowest temperature ~5K, which is far below glass transition temperature (T_g=313K) to a temperature above bulk T_g for the evaluation of temperature dependence of means square displacement ($\langle u^2 \rangle$). Then we also measured QENS spectra at 293K, 333K, 353K, 373K, 393K, 413K, 433K, 453K and 473K with an energy resolution of 3.0 μeV.

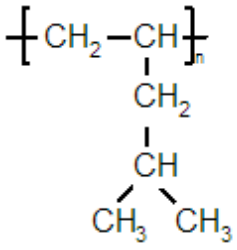

Fig.1 Chemical structure of P4M1P.

Results and discussion

Fig.2 indicates the temperature dependence of $\langle u^2 \rangle$ obtained from P4MP1 sample. In the temperature range below ~170K the observed $\langle u^2 \rangle$ is proportional to T, suggesting that the motion below ~170K is harmonic. On the other hand above ~170K, which is far below T_g $\langle u^2 \rangle$ starts to deviate from the linear relationship and a steep increase of T_g was observed. It implies the onset of anharmonic motion. Such a rapid increase of $\langle u^2 \rangle$ at the temperature below T_g have already been reported for conventional amorphous

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

amorphous polymers like polystyrene (PS), polybutadiene (PB), polyisobutylene (PIB) and so on and it was concluded that the origin of anharmonic motion below bulk T_g wasattributed to localized process or so-called fast process. Hence it is supposed that the onset of anharmonic motion at around 170K might be originated from fast process for P4MP1 as well. With further increasing temperature the other steep increase of $\langle u^2 \rangle$ was observed at around 310K and this temperature coincided with bulk T_g determined by DSC. Therefore a steep increase of $\langle u^2 \rangle$ observed at round 310K was attributed to a detection of Tg of P4MP1 with DNA spectrometer. Interestingly we again observed another steep increase of $\langle u^2 \rangle$ at around 410K, which is about 100K above T_g. We could not understand the physical origin for a steep increase of $\langle u^2 \rangle$ at 410K adequately from the temperature dependence of $\langle u^2 \rangle$ only. Hence we focused on spectra measured at the temperatures both below and above T_g to extract the physical interpretation for a drastic increase of $\langle u^2 \rangle$ at around 410K and the observed QENS spectra at Q=1.125 Å^{-1} are summarized in Fig. 3. Focusing on the observed spectra, we could surely observe QENS for all the temperatures examined and this observation is consistent with the temperature dependence of $\langle u^2 \rangle$. Up to 393K the observed dynamics scattering laws are well fitted by with a model function (model function 1) given by the sum of a delta function, single Lorentzian and flat background. It implies that a single relaxational process exited with the energy resolution of 3 μeV. We could not observe a clear Q dependence of relaxation rate and only a quite weak temperature dependence of half-width at half maximum for the observed dynamics are shown in Fig.4, indicating that the observed dynamics is a localized process.

The observed $S(Q, \omega)$ profiles measured at the temperatures above 393K were not well fitted by the model function 1 due to the broadening of central component. Hence we tried to fit the observed spectra with another model function (model function 2) given by the sum of a delta function and Havriliak-Negami function (or Fourier transformed KWW function) under the constraint that beta values were fixed to 0.5. It was found that model function 2 could describe the observed QENS spectra well, indicating that the observed dynamics above 413K was ascribed to alpha process, which plays a main role for glass transition. Hence it was supposed that the abrupt increase of $\langle u^2 \rangle$ at around 413K is related to the detection of alpha process with the energy resolution of 3μeV measurements. More detailed analysis is still on progress.

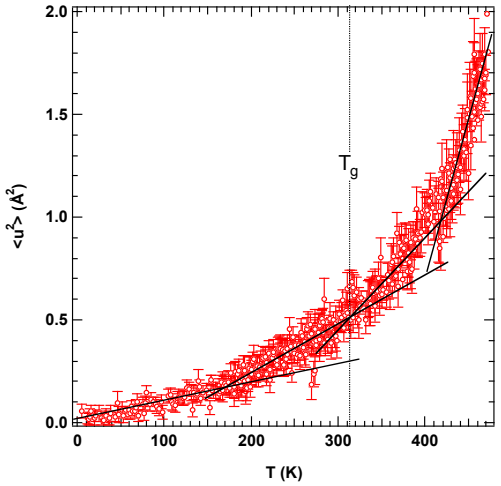

Fig. 2 Temperature dependence of $\langle u^2 \rangle$ observed for P4MP1 with the energy resolution of 3μeV.

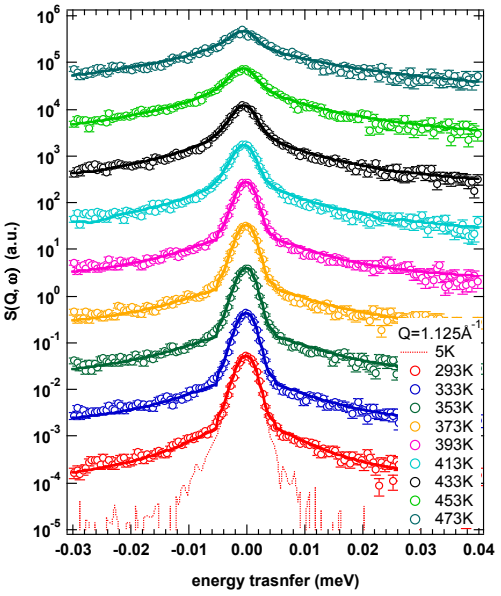

Fig. 3 Dynamics scattering laws $S(Q, \omega)$ observed at the temperatures both above and below T_g and dotted line corresponds to resolution function measured at 5K.

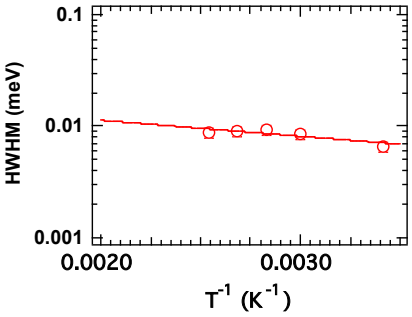

Fig. 4 Temperature dependence of an Half width at half maximum (HWHM) observed for QENS below 393K fitted with model function 1.