（ ※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 2015/1/4 承認者 Approver Jun-ichi. Suzuki 提出日 Date of Report 2014/7/25
課題番号 Project 2013B0011 実験課題名 Title of experiment **Effects of molecular weights on shish-kebab formation** 実験責任者名 Name of principal investigator Toshiji Kanaya 所属 Affiliation Kyoto University	装置責任者 Name of Instrument scientist Shin-ichi Takada, Jun-ichi Suzuki 装置名 Name of Instrument/（BL No.） TAIKAN/BL15 実施日 Date of Experiment 2014/3/16 10:00- 2014/3/19 9:00

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.

Blends of d-PE (Mw=600,000; 97%) and h-PE (Mw =2M, 1M, 300k, 100k, 58k ; 3%)

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.

In flow-induced crystallization processes the so-called shish-kebab structure is often observed in the morphology, which consists of a long central core (shish: extended chain crystal) surrounded by lamellar crystals (kebabs). It is believed that the shish-kebab is the structure origin of the ultra-high strength and modulus of fibers, so extensive studies have been performed to elucidate the morphology and the processes of formation.

It was believed that high molecular weight component enhances the shish formation because the sample including more high molecular component had higher modulus than those including less high molecular component. In order to confirm this idea, we performed small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS) experiments on a drawn polyethylene blend of high molecular weight protonated polyethylene (HMW h-PE, Mw=2,000,000, 2.8%) and low molecular weight deuterated polyethylene (d-PE, Mw~20,000, 97.2%) in our previous experiment. It was found that HMW h-PE formed shish.

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

However, in the same month in the same year (May, 2007), completely different experimental results were published on blends of deuterated and protonated isotactic polypropylene (d-iPP and h-iPP) by Sumitomo Chem. Co. group. It was shown that low molecular weight component was included in the shish more than high molecular weight component. We decided to perform SANS and SAXS experiments to confirm the effects of low and high molecular weight components on shish-kebab formation for blends of d-PE (Mw=600,000; 97%) and h-PE (Mw =2M, 1M, 300k, 100k, 58k; 3%). The samples were drawn with very slow drawing rate of 6 μm/s at 125 °C. It was found that shish scattering in SANS is stronger for blend including lower molecular weight h-PE, showing the similar tendency with the results of Sumitomo Chem. Co. Group.

We interpreted this result on the basis of in-situ drawing experiment on the same sample [G. Matsuba et al., *Polymer J.* 44, online publication 1 Aug. 2012.] as follows at the moment. In the beginning of the drawing process, high molecular weight component forms the shish because it can be easily stretched due to the entanglement. In the late stage polymer chains included in kebab (lamellar crystals) are merged into the shish and the kebab disappears. This disappearance of kebab was observed in TEM experiments [T. Hashimoto, et al., *Macromolecules* **43**, 6542 (2010)]. Key point of this interpretation is that the merging process of polymer chains into shish from kebab is harder for high molecular weight component than for lower molecular weight component because the higher molecular components are entangled and go though several lamellar crystals. This was shown in a cartoon of Figure 1.

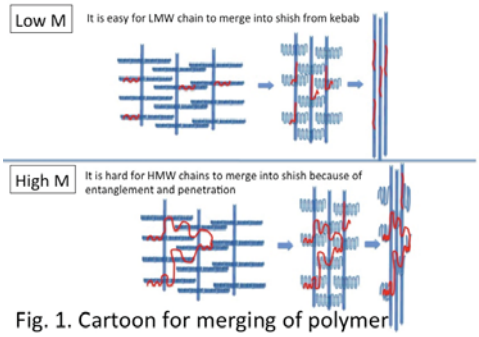

Fig. 1. Cartoon for merging of polymer chains into shish from kebab.

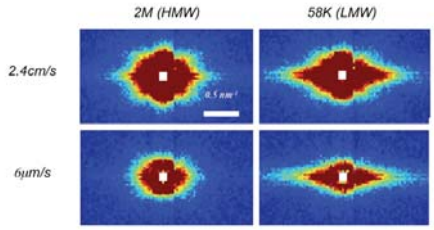

Figure 2. 2D SANS pattern from Blends of d-PE (Mw=600,000; 97%) and h-PE (Mw =2M, 58k ; 3%) for two drawing rates (2.4 cm/s, 6μm/s).

If this mechanism is correct, the relaxation rate of polymer chains must be faster than the drawing rate because polymer chains cannot follow the drawing if they are drawn at a rate faster than the relaxation. This means that there must be a critical drawing rate *R*c for this proposed mechanism. In order to confirm the proposed mechanism we started our experiments.

In the last experiment (2013A), however, the beam stopped at 8 hours after starting the measurement. Therefore, unfortunately our experiments were not finished, but only four spectra were obtained, which is shown in Figure 2.

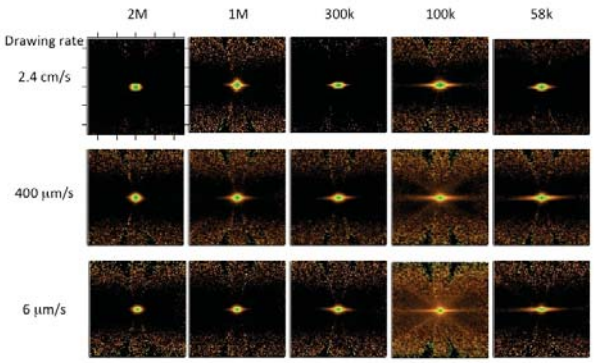

Figure 3. Dependences of 2D SANS patterns on molecular weight and draw rate. Drawing ratio is 7.0

In the present experiment we performed ex-situ measurements on the blend listed above. The results are shown in Figure 3. It was found in this systematic experiments that in the late stage of drawing LMW component is in the shish more than HMW, and compared between slow and fast drawing rates, LMW component is in the shish more than HMW in the slower drawing rate. These results qualitatively support our predictions. However, due to the lack of machine time it was impossible to do in-situ measurements. We will do the in-situ experiments in 2014B to finalize our work.