CROSS TOKAI **Experimental Report** J-PARC	承認日 Date of Approval 承認者 Approver 提出日 Date of Report
課題番号 Project No. 2017A0229 実験課題名 Title of experiment Critical fluctuation at the polymerization transition of liquid sulfur 実験責任者名 Name of principal investigator Yoshifumi Sakaguchi 所属 Affiliation CROSS	装置責任者 Name of Instrument scientist Jun-ichi Suzuki 装置名 Name of Instrument/(BL No.) TAIKAN (BL15) 実施日 Date of Experiment May 11-13, 2017

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.

Sulfur (liquid in the quartz glass cell)

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 method:

Liquid sulfur consists of S_8 rings just above the melting temperature of 119 °C, and the polymerization occurs at 159 °C. Although it is composed of only one element, it was pointed out at the beginning of the 20th century from the measurement of the freezing point depression that there was an insoluble sulfur to liquid sulfur composed of S_8 rings. Recently, we showed from the photo-induced transient optical absorption measurement that the insoluble sulfur was thermally generated or generated by a light illumination, and that the polymerization transition could be regarded as a critical phenomenon, in which the concentration of the insoluble sulfur reached a certain value [1]. According to our preliminary experiment of light scattering using a He-Ne laser, we observed fluctuation in the light scattering below the polymerization temperature, and we inferred that it must be a critical fluctuation. In this experiment, we try to observe the critical fluctuation by means of neutron scattering technique. The temperature control was made by using the furnace specially designed for the SANS measurement (Fig.1). To eliminate unwanted background scattering, the B_4C collimator with a diameter of 4 mm was used. A quartz glass cell with an inner diameter of 10 mm and a thickness of 5 mm was used for the experiment. The proton beam power in the measurement was 150 kW.

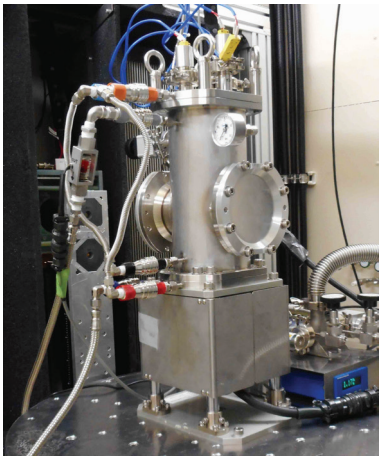

Fig. 1

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

Experimental results:

Fig. 2 shows the semi-logarithmic plots of the small-angle neutron scattering of liquid sulfur at several temperatures. As shown in the figure, a large SANS intensity was not observed in the measured Q region, and the temperature-dependence of the SANS intensity was not evident. However, at 160 °C, there is a difference in the SANS intensity between the heating and cooling processes in the Q range from 0.3 to 0.8 ($Å^{-1}$). This would suggest a slow structural relaxation at the temperature region. Also, the SANS intensity in Q < 0.2 ($Å^{-1}$) at 140 °C in the cooling process seems to be a little bit larger compared to those at other temperatures. This may be related to the fluctuation of the insoluble sulfur, which appears below the polymerization temperature. Fig. 3 shows the double logarithmic plots. An increase of the SANS intensity at lower Q region is clearly observed at 160 °C in the cooling process and the SANS intensity seems to follow the power law with the index of −3. This may be related to the appearance of the long polymeric chains in the temperature region. Overall, there are some findings on the SANS profiles of liquid sulfur. However, the S/N ratio was not enough to conclude these possibilities. In the present measurement, the collimator with a diameter of 4 mm was used to eliminate the background from the alumina tube of the furnace. This reduced the scattering intensity very much. The data could be improved if the neutron beam size was much larger. We are now preparing a new furnace which can accept much larger neutron beam. We will also try to improve in the analysis. According to our observation in the experiment, the SANS intensity seemed to be larger during heating or cooling process before reaching the equilibrium. This may be related to the slow dynamics of the system, and we will also analyze from such dynamic point of view.

[1] Y. Sakaguchi and K. Tamura, *Jpn. J. Polym. Sci. Tech.* (*Kobunshi Ronbunshu*) **64** (2007) 830.

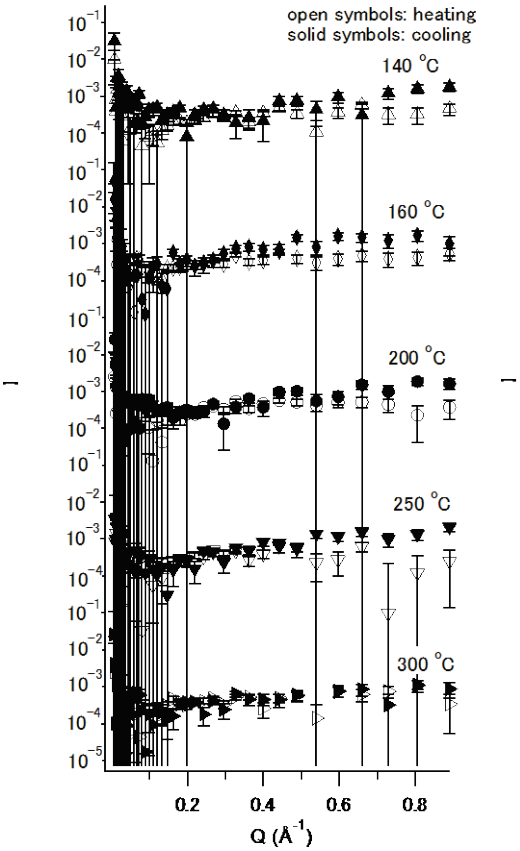

Fig. 2

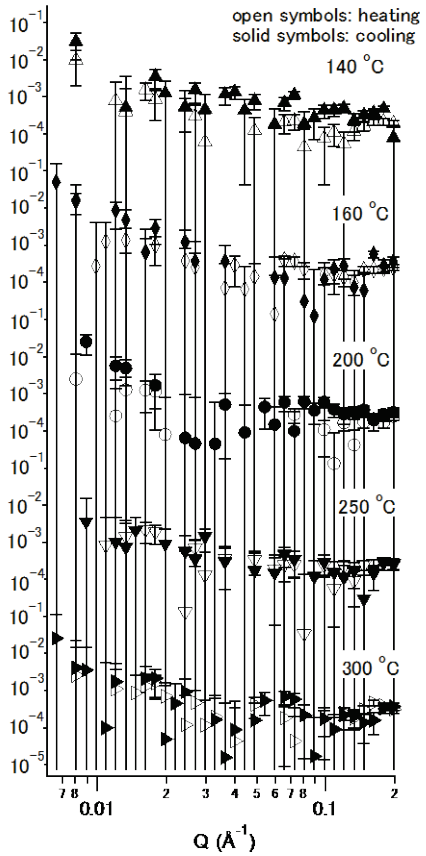

Fig.3