（ ※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 2017/12/9 承認者 Approver Jun-ichi Suzuki 提出日 Date of Report 2017/ 11/30
課題番号 Project No. 2016A0198 実験課題名 Title of experiment Study on cocrystallization of syndiotactic polystyrene with polyethylene glycol oligomers by simultaneous neutron scattering / vibrational spectroscopy measurement 実験責任者名 Name of principal investigator Fumitoshi Kaneko 所属 Affiliation Graduate School of Science, Osaka University	装置責任者 Name of responsible person Hiroki Iwase 装置名 Name of Instrument/(BL No.) TAIKSAN/(BL15) 実施日 Date of Experiment 26.12.2016–29.12.2016

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.

Solutions were prepared using the following chemicals

[Solutes]

protonated polyethylene glycol (−CH2CH2O−)n :h−PEG

deuterated polyethylene glycol (−CD2CD2O−)n :d−PEG

protonated syndiotactic polystylene (−CH2CHC6H5−)n: h−sPS

deuterated syndiotactic polystyrene (−CD2CDC6D5−)n: d−sPS

[Solvents]

protonated tetrahydrofura (C4H8O) and deuterated tetrahydrofuran (C4D8O):h−THF and d−THF

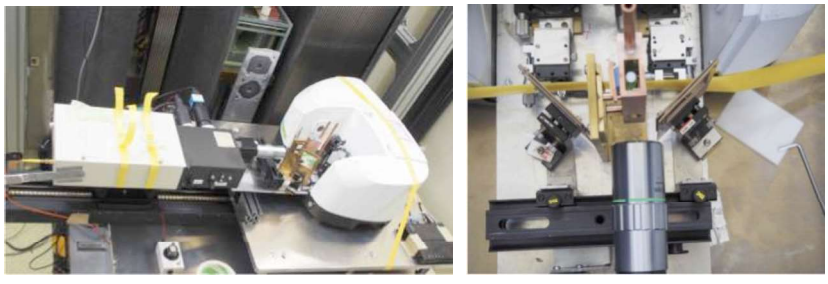
[Solutions]

(a) h−sPS (2.8wt%) in d−THG, (b) h−PEG(1 wt%) in d−THF, (c) h−sPS(2.8wt%) and d−PEG(1 wt%) in d, h−mixed THF, (d) d−sPS(2.8wt%) and h−PEG(1 wt%) in d,h−THF, (e) h−sPS(2.8wt%) and h−PEG(1 wt%) in d−THF.

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 this experiment, we tried to conduct simultaneous measurements of SANS/WANS together with FTIR and Raman spectroscopy. For this purpose, we made an experimental setup on the sample stage of TAIKAN, as shown in Figure 1.



(a) (b)

Fig 1. Experimental setup at the sample stage of TAIKAN. (a) Overall view of the setup, where an Raman spectrometer and an FTIR one are arranged at the left and right sides. (b) The optical system and the sample cell.

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

Four kinds of solutions (a)–(d) listed above were employed for the simultaneous measurements. Solutions (a) and (b) were used to monitor the behavior of PEG and sPS in a single–solute solution, and solutions (c), (d) and (e) were used to monitor the behavior of sPS in a two–solute solution, in particular, to study how each component interacts in a two–solution solution, giving a change in the gelation process. Each solution was at first heated above 100°C to clear structural memories of the solution, and then cooled to 70 and 40°C. The structural changes were followed with neutron scattering and vibrational spectroscopy.

We succeeded to measure the neutron scattering profile, FTIR spectrum and Raman spectrum simultaneously. However, it was found that the performance of the present Raman system was not enough to get the structural information about the solutes in these solutions. The efficiency of the objective lens with a long working distance, which was used to reduce the amount of exposure to the scattered neutron beams for the sample, was less than that of the ordinary objective lens with short distance. Another problem was that the weak signals coming from the solute polymers, which were minor components of the solutions, were overwhelmed by the strong signals of the solvent THF.

As for the SANS data, we have confirmed the different behaviors of PEG and sPS in these solutions. As shown in Figure 2_1, solutions (a) and (b) at 77°C showed a slope of −5/3 in the log(I)–log(Q) plot, suggesting that both PEG and sPS chains are in a swollen chain state in these solution. However, when cooled to 40°C, these solution showed different behaviors, as shown in Fig. 2_2. The intensity of solution (a) increased significantly in low Q region, whereas that of solution (of both sPS and PEG chains b) remained almost unchanged, suggesting no significant conformational changes. The slope of solution (a) around Q around Q = 10^{-2}Å^{-1} became close to −1, suggesting that the sPS chain had become a rod like structure. Considering that solution (a) forms a gel around this temperature, the conformational change to a regular helical conformation would be accompanied with the formation of tiny crystallites that act as binding points of the gel network.

Similar behaviors were observed for both sPS and PEG components in the two–solute (sPS, PEG) system. As shown in Fig 2_3, the sPS chain carried out a conformational change to a regular helices, whereas the PEG chains did not show any significant conformational changes, as observed in solutions (a) and (b). However, the gelation proceeded faster in two–solute solutions (c) to (e) than solution (a). The IR spectral changes and the SANS intensity changes on gelation were larger in the two–solute systems, which suggests that the PEG component assists the conformational ordering of the sPS component.

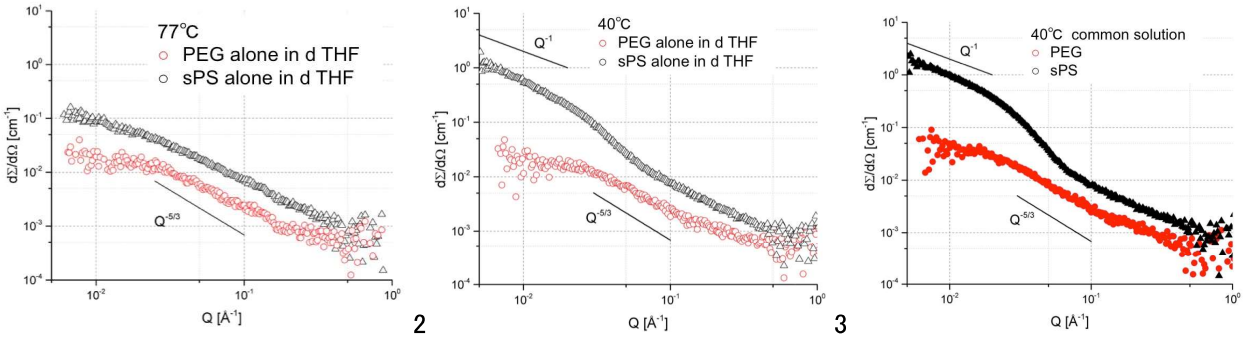


Fig. 2. SANS curves due to SPS and PEG components in one-solute solution at 77°C (1) and at 40°C (2) and two-solute solution at 40°C (3).