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Development of a simultaneous SANS / FTIR measuring system and its application to polymer cocrystals

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Abstract. In order to provide plenty of structure information which would assist in the analysis and interpretation of small angle neutron scattering (SANS) profile, a novel method for the simultaneous time-resolved measurement of SANS and Fourier transform infrared (FTIR) spectroscopy has been developed. The method was realized by building a device consisting of a portable FTIR spectrometer and an optical system equipped with two aluminum coated quartz plates that are fully transparent to neutron beams but play as mirrors for infrared radiation. The optical system allows both a neutron beam and an infrared beam pass through the same position of a test specimen coaxially. The device was installed on a small angle neutron diffractometer, KWS2 of the Jülich Centre for Neutron Science (JCNS) outstation at Heinz Maier-Leibnitz Center (MLZ) in Garching, Germany. In order to check the performance of this simultaneous measuring system, the structural changes in the cocrystals of syndiotactic polystyrene during the course of heating were followed. It has been confirmed that FTIR spectra measured in parallel are able to provide information about the behavior of each component and also useful to grasp in real time what is actually happening in the sample system.

1. Introduction

Small angle neutron scattering (SANS) has been employed in research that aims at analyzing the mesoscopic scale structures. In combination with partial deuteration technique, SANS is able to characterize the structure of a specific part in a complex system, which makes it unsubstitutable with any other method for structural analysis. SANS has established its unique position as a powerful tool for structural investigation of soft-matter and biological systems. Furthermore, owing to the technological development in instrumentation in recent years such as detectors and neutron guides, SANS has extended its presence not only in the research of static structure but also in the research of time-dependent structure evolution.

The scattering pattern of SANS is determined by the scattering length density (SLD) profile in the object under study. Therefore, it is of great difficulty to derive the sole solution for the arrangement of constituent components only from the scattering pattern of SANS, in particular, when the system of interest is a multicomponent system [1, 2]. This issue increases in importance as the system under research becomes more complicated. If we get any other structural information from the same system, it would reduce greatly the difficulty of analyzing the SANS data.

For this purpose, the simultaneity between data obtained by different kinds of methods is considered to be crucial in the study of time-evolving structure changes of soft materials and biological samples. These systems are so sensitive that it is difficult to reproduce the time course of structural changes completely. Therefore, it is desirable to obtain two or more different kinds of structural information simultaneously from the same sample. Vibrational spectroscopy is a strong candidate for this purpose; indeed it has been employed as a complementary tool of X-ray and neutron diffractometry for investigating the structure of polymer systems. It provides information about the concentration and conformational state of each chemical species in a measuring object. Furthermore, the partial deuteration method for SANS experiments provides another advantage; the vibrational modes of deuterated components shift to low frequencies greatly, eliminating the overlap of the bands due to different chemical species, which makes the analysis and interpretation of spectral data easier. As for synchrotron radiation, simultaneous analyzes by X-ray scattering and Fourier transform infrared (FTIR) spectroscopy have been developed so far [3, 4, 5]. Similarly, the introduction of FTIR spectroscopy to SANS would produce a fruitful methodology for such a simultaneous measurement system.

Owing to a high throughput optical system, a highly sensitive detector, and advanced hardware and software design, it is easy to follow the time evolution of infrared spectra with a compact FTIR spectrometer [6, 7]. Using these advantages of FTIR spectroscopy, we have been developing a simultaneous SANS/FTIR measuring system at the SANS diffractometer KWS2 of the Jülich Centre for Neutron Science (JCNS), outstation at Heinz Maier-Leibnitz Center (MLZ) [8, 9].

In this paper, we are going to present the concept and actual construction of the simultaneous measuring system and also some experimental examples concerning the cocrystals of syndiotactic polystyrene (sPS). sPS is a stereoregular polymer, which has a unique property to form cocrystals with a variety of chemical compounds, by including them into the crystalline lattice. This unprecedented property attracts a wide range of attention, in particular, in the viewpoint of material development [10, 11]. In this research, we studied how the molecular weight of guest molecules affects the structural changes of the sPS cocrystal system on heating process. We will show how the FTIR spectrum measured in parallel with SANS is valuable for interpreting SANS profile changes. It is able to provide how each component in the sample behaves and also monitor chemical structural changes in real time, including cases that happen accidentally, in the sample being measured.

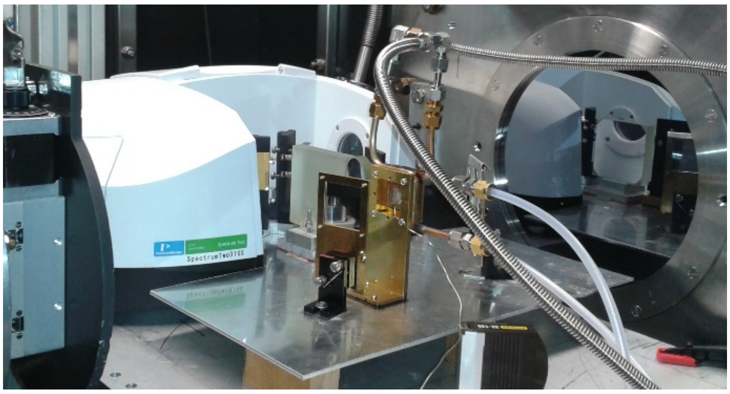


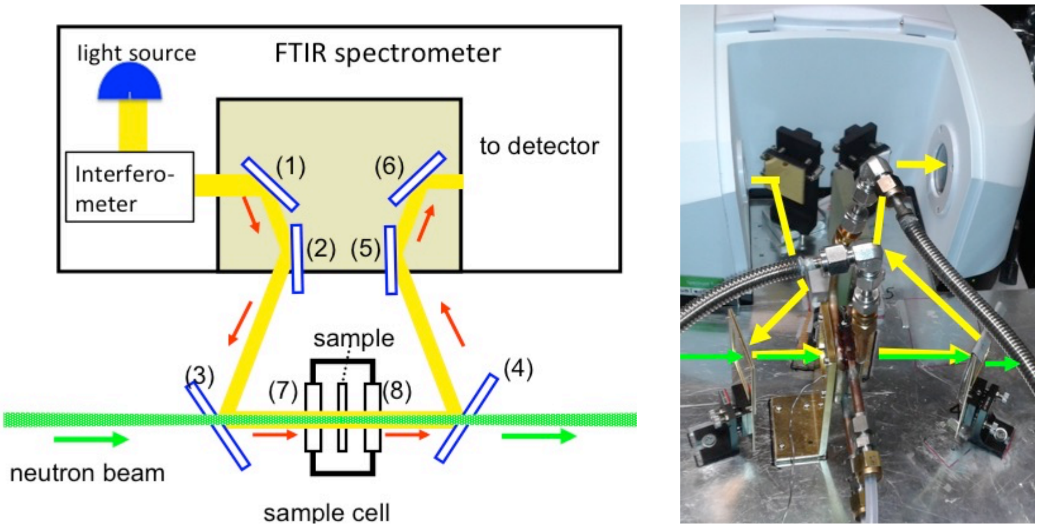
Figure 1. Experimental setup for simultaneous SANS/FTIR measuring system installed at the SANS diffractometer KWS-2 in MLZ (Garching, Germany).

2. Simultaneous SANS/FTIR measurement system

The device for simultaneous SANS/FTIR measuring system consists of a compact portable FTIR spectrometer (PerkinElmer, Spectrum Two) and an optical system of our own making. The device was designed to be installed in the sample chamber of a SANS instrument as show in Figure 1. The concept of the simultaneous system is depicted in Figure 2(a) and the actual construction of the optical system is given in Figure 2(b). The optical system consists of six mirrors (optical elements 1 to 6), which can be grouped into two types by function. Elements 3 and 4, which are irradiated by both the neutron beam (green line) and infrared beam (yellow line), work as a beam mixer and selector, respectively. They transmit the neutron beam efficiently but act as mirrors to reflect the infrared beam. To achieve such functions, elements 3 and 4 are made by aluminum vacuum deposition on optical grade synthetic quartz plates with thickness of 0.5 mm using the characteristics of aluminum and quartz: both are transparent to neutron beam, but the surface layer of aluminum reflects infrared radiation with high efficiency. The other four elements work as mirrors only for the infrared beam. As for the windows (elements 7 and 8) of the sample cell with a brass body wound with a copper tube to temperature control, we used KBr plates of 2 mm thickness because KBr is transparent to in the middle infrared region (4000-400 cm^{-1}) and also has a relatively good transparency to neutron beam.

The two beams in the system are made to run on the same line by element 3 and pass through the same sample position coaxially, and then they are separated from each other with element 4. Each separated beam goes to its own detector system.

Although the large part of the IR path is in open air, the influence of H_2O and CO_2 in the air is efficiently removed through the digital filtering algorithm of the FTIR spectrometer.



(a) (b)

Figure 2. (a) Schematic drawing of the optical system for simultaneous SANS / FTIR measuring system. Parts 1 to 6 are mirrors and parts 7 and 8 are windows of the sample cell. The infrared and neutron beams are represented with yellow and green lines. (b) The photographic image of the optical system.

3. Experimental

3.1. Sample

In order to confirm the performance of the simultaneous measurement system, the specimens of sPS cocrystal with polyethylene glycol dimethyl ethers (PEGDMEs) were prepared by the following procedures. In order to depress strong incoherent scattering from the sPS matrix, fully deuterated sPS (d-sPS) (Mw=1.1×105 and Mw/Mn = 1.9) was synthesized according to the coordination polymerization developed by Ishihara et al. [12], using fully deuterated styrene with purity more than 98% purchased from Cambridge Isotope Lab. Two kinds of PEGDMEs with different molecular weights were used. One was a PEGDME with molecular weight of 178 (PEGDME178) and the other was a PEGDME with molecular weight of 500 (PEGDME500), both of which were purchased from Sigma-Aldrich and used without further purification.

Uniaxially oriented amorphous d-sPS films about 50 μm thick were prepared by drawing melt quenched amorphous d-sPS films four times in an oil bath kept at 100°C, and then the films were exposed to a vapor of chloroform to obtain sPS/chloroform cocrystal films. The cocrystal films were soaked into liquid PEGDME178 for one day and then kept in a vacuum oven at 40°C for an hour, giving uniaxially oriented sPS/PEGDME178 cocrystal films. The samples of sPS/PEGDME500 cocrystal were prepared by the same procedure, except that liquid PEGDME178 was substituted with a PEGDME500/chloroform mixture at about 1:1 in weight ratio.

3.2. Measurements

All the simultaneous SANS/FTIR measurements were carried out by using the KWS2 diffractometer of the Jülich Centre for Neutron Science (JCNS), outstation at Heinz Maier-Leibnitz Center (MLZ) in Garching, Germany. Scattering data were obtained using a 2D detector with active area of 60 × 60 cm^2 and 128 × 128 channels. A wavelength λ= 0.7 nm ($\Delta\lambda/\lambda$ = 20%) and a sample-to-detector distance of 4 m and 1.35 m were chosen. The typical measured sample area was about 5 × 5 mm^2. The data accumulation time for each data point was 15 min. The temperature of the sample cell was controlled within the accuracy of ±0.2 °C by circulating thermostated oil. The sample 3 kept under a slow flow of air. Transmission IR spectra were taken at a resolution of 2 cm^{-1} and a 10 min interval. The average accumulation time and the number of scans were 10 min and 128, respectively. For measuring time dependence of IR spectra and analyzing them, a commercially available software (PerkinElmer, Timebase) is employed.

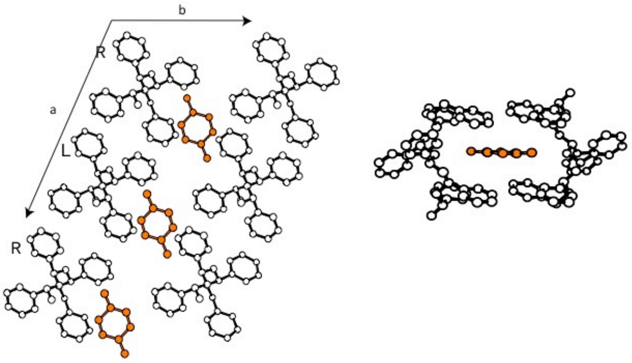


Figure 3. A model of sPS-cocrystal structure (monoclinic δ intercalate cocrystal with toluene) [12]. Left: projection onto the *ab* plane. Right: side view of a cavity containing toluene.

4. Results and Discussion

4.1. Influence of guest molecular weight on the behavior of sPS/PEGDME cocrystals on heating

Although several sPS cocrystal structures with different crystal systems and cavity shapes have been reported so far, the guest molecules are held between regularly arranged sPS helices taking TTGG conformation [10, 11]. The monoclinic δ clathrate structure with two cavities per unit cell (Figure 3 [12]) has been most frequently observed. According to the previous study, the sPS/PEGDME cocrystals prepared by the guest exchange procedure are assumed to maintain this type of structure [13]. The crystalline lamellae of uniaxially oriented sPS cocrystals are stacked in the drawing direction with a repeat period of about 10 nm. The lamellar stacking gives two lamellar reflections in

2D SANS images. Under the present experimental condition that sPS cocrystal film sample consists of fully protonated guest PEGDME and fully deuterated sPS (d-sPS), the distribution of PEGDME molecules principally determines the 2D SANS profile.

SANS profile changes on heating process are obviously different between the two kinds of d-sPS/PEGDME cocrystals with different guest size, as shown in Figure 4. As for d-sPS/PEGDME178 cocrystal, the lamellar reflection remarkably decreases in intensity as temperature increases up to 80 ˚C, leading to their almost annihilation. A further heating from 100 to 135 ˚C brings about the reappearance and gradual intensity increase of the two reflections. On the contrary, the lamellar reflection increases in intensity with temperature for d-sPS/PEGDME500 cocrystal.

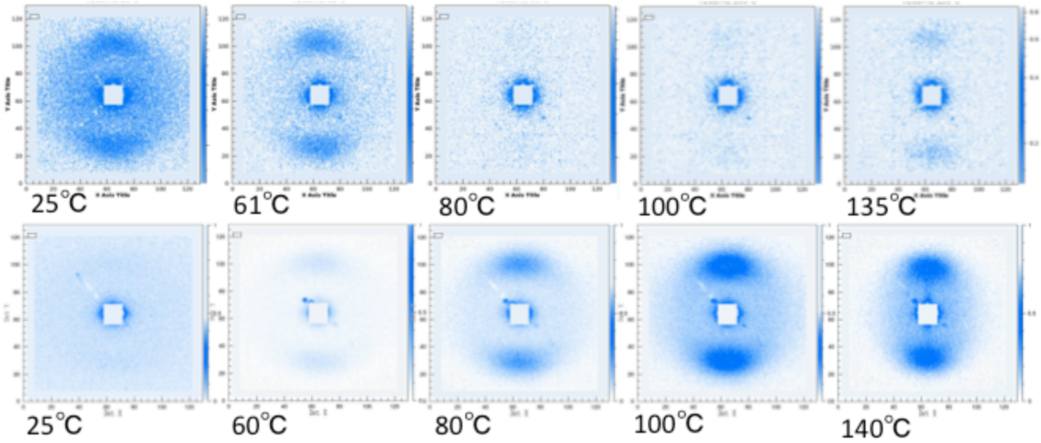


Figure 4. Temperature dependence of SANS 2D images. Top: d-sPS/PEGDME178 and bottom: d-sPS/PEGDME500.

From FTIR spectra measured in parallel with SANS 2D images (Figure 5), it can be seen that the PEGDME content behaves in a completely different manner between the two kinds of sPS cocrystals. As for d-sPS/PEGDME178 cocrystal, the bands due to host d-sPS, such as C-D stretch in the region of 2300 to 2150 cm^{-1} and C=C stretch around 1568 cm^{-1}, do not show any significant intensity changes during the course of temperature change, whereas the bands ascribed to PEGDME178, such as C-H stretch around 2874 cm^{-1} and C-O stretch around 1106 cm^{-1}, decrease in intensity with an increase in temperature. As for d-sPS/PEGDME500 cocrystal, not only the bands due to host d-sPS but also the ones due to guest PEGDME500 do not show remarkable intensity changes during the course of heating, except a slight intensity decrease of the guest bands. These results suggest that there is no significant change as to the d-sPS content in both d-sPS cocrystals and only the PEGDME178 component continues to decrease remarkably during this heating process.

Since the volatility of PEGDME molecules greatly depends on molecular weight, it seems that the nearly the three times difference in molecular weight drastically changes the desorption behavior of PEGDME component from the d-sPS/PEGDME cocrystal film, which consists of two processes, the migration from the crystalline region to the amorphous region and the migration from the amorphous region to the outside of the film. At the moment, we have the following view about the desorption behavior based on the SANS and FTIR data.

As for d-sPS/PEGDME178 cocrystal, the two kinds of migration take place smoothly, which results in a smooth decrease in concentration of the guest molecules both in the crystalline and amorphous region, as schematically shown in Figure 6 (top). Since the distribution of the protonated guest is the main factor for the contrast in scattering length density (SLD) between the amorphous and crystalline regions, the SLD contrast would decrease significantly by the smooth guest desorption, which is consistent with the SANS experimental observation. The slight intensity increase in the highest temperature region can be ascribed to the transformation to the γ phase, whose mass density is higher than that of the amorphous region, leading to a slight resurgence in the SLD contrast between the crystalline and amorphous regions.

On the other hand, the guest migration from the crystallization to the amorphous region takes place principally for d-sPS/PEGDME500 film, and therefore, the guest concentration in the amorphous region monotonously increase with temperature. The marked intensity increase at the high temperatures is attributable to an increase in the SLD contrast caused by this guest, as shown in Figure 6 (bottom).

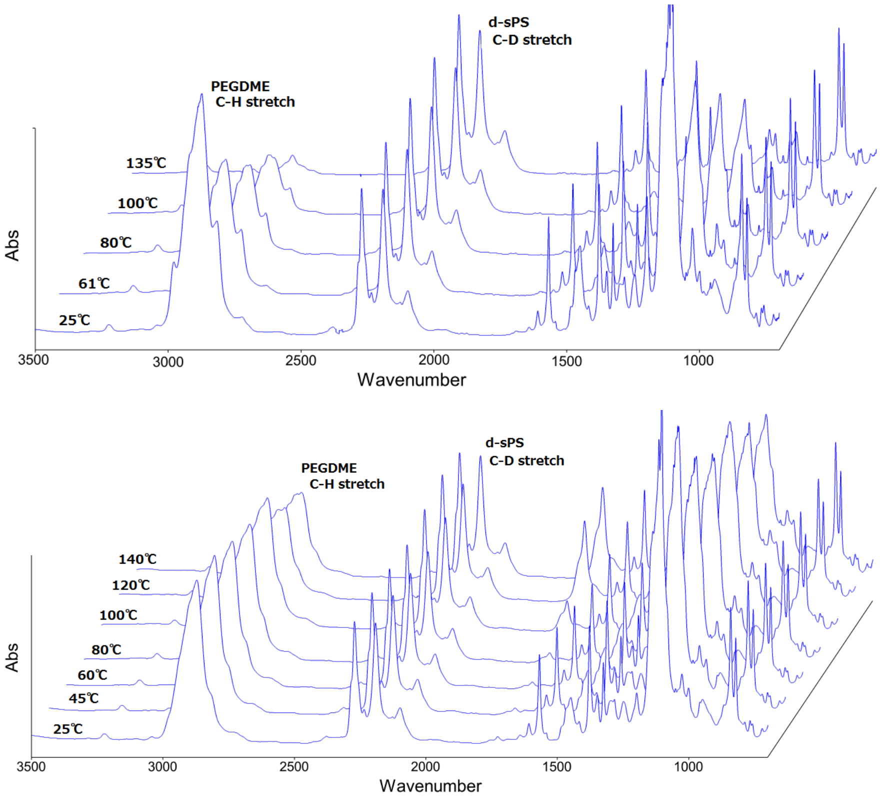


Figure 5. FTIR spectral changes measured in parallel with SANS measurements.
Top: d-sPS/PEGDME178 and bottom: d-sPS/PEG500.

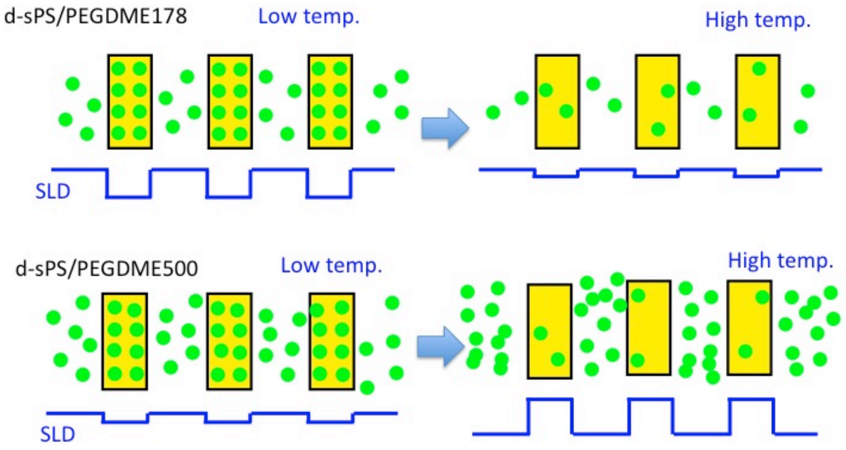


Figure 6. Schematic representation for temperature dependent distribution change of guest molecules. The solid state of d-sPS/PEGDME cocrystal is depicted as a one-dimensional array of crystalline lamellae (yellow box) and interlamellar amorphous regions (white parts). The green circles represent

guest PEGDME molecules. The blue rectangle wave below represents the variation of scattering length density between the crystalline and amorphous regions.

4.2. Decomposition of sPS/PEGDME500 cocrystals on heating

As described in the previous section, the bands due to the guest component show a slight intensity decrease on the heating process of the d-sPS/PEGDME500. In order to look into what happens in the cocrystal sample, the IR spectra measured in parallel with SANS have been checked. A band around 1728 cm^{-1} appears and clearly increases in intensity with temperature, in particular above 80°C, as shown in Figure 7 (right). The 1728 cm^{-1} band can be assigned to the carbonyl stretch mode ν(C=O) due to the aldehyde group of low-mass products by the thermal decomposition of polyethylene glycol, which starts even in relatively moderate conditions [14, 15]. Such low mass products would gradually dissipate into the outside. Therefore, it can be inferred that a small amount of PEGDME500 is lost from the cocrystal film owing the thermal decomposition at elevated temperature, which results in the intensity decrease of the C-H stretch band.

A similar thermal decomposition would occur for PEGDME178 component. However, the most part of the guest molecules dissipate smoothly to the outside because of its low molecular weight before the temperature becomes high enough for the thermal decomposition, and accordingly the band due to aldehyde group did not appear appreciably on the heating process of the d-sPS/PEGDME178 cocrystal, as shown in Figure 7 (left).

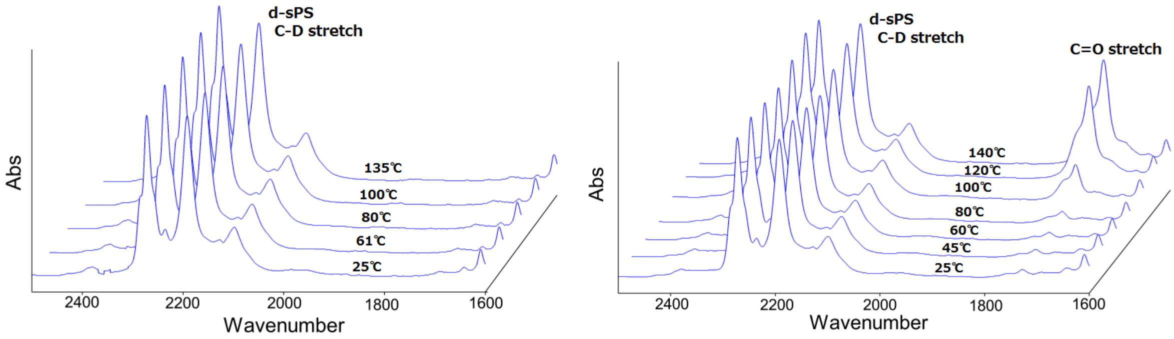


Figure 7. Temperature dependent IR spectral changes of sPS/PEGDME178 (left) and sPS/PEGDME500 (right) cocrystals.

Conclusion

A novel method for the simultaneous time-resolved measurement of SANS and FTIR spectroscopy has been developed. Since a change in chemical composition and chemical structure is sensitively reflected in FTIR spectra, the information obtained by FTIR spectrocopy is helpful to interpret SANS scattering profiles. This system is also able to detect chemical degradation happening in the sample on site, which is difficult to be noticed by SANS measurements. The simultaneous measuring system would be useful for research on a variety of multi-component systems, such as, polymer composites and polymner blends, and other kinds of materials containing non-hydrogeneous parts which are less visible by SANS. Furthermore, it can provide the information about the conformational changes of chemical compounds in different conditions, which would be useful for the analysis of SANS profile.

References

[1] Roe R-J 2000 *Methods of X-Ray and Neutron Scattering in Polymer Science* (New York: Oxford).

[2] Higgins J S and Benoit H C 1997 *Polymers and Neutron Scattering* (New York: Oxford).
[3] Naylor S *et al* 1995. *Nucl. Instrum. Methods Phys. Res., Sect. B Res., Sect.* B **97** 253.
[4] Innocenzi P *et al* 2007 *J. Phys. Chem.* C **111** 5345.
[5] Ratri P J and Tashiro K 2013 *Polym. J.* **45** 1019.
[6] Koenig J L 1999 *Spectroscopy of Polymers* (New York, Elsevior).
[7] Griffiths P R and de Haseth J A 2007 *Fourier Transform Infrared Spectrometry* (New Jersey: Wiley).
[8] Kaneko F *et al* 2015 *Chem. Lett.* **44** 497.
[9] Kaneko F *et al* 2015 *MLZ News* **14** 12.
[10] Guerra G *et al* 2009 *Preparation, structure, properties, and applications of co-crystals and nanoporous crystalline phases of syndiotactic polystyrene* (Syndiotactic polystyrene) ed Schellenberg J (Hoboken, Wiley).
[11] Guerra G *et al* 2012 *J. Polym. Sci. Polym. Phys.* **50** 305.
[12] Chatani Y *et al* 1992 *Polymer* **33** 488.
[13] Kaneko F and Sasaki K 2011 *Macromol. Rapid Commun.* **32** 988.
[14] Bortel E *et al* 1979 *Macromol. Chem.* **180** 2491.
[15] Han S *et al* 1996 *Polymer* **38** 317.