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Editor's Choice

Development of a Simultaneous SANS/FTIR Measuring System

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A novel method for the simultaneous measurement of small-angle neutron scattering and Fourier transform infrared spectroscopy (SANS/FTIR) has been developed. The method was realized by building a device consisting of a portable FTIR spectrometer and an optical system that allows both a neutron beam and an infrared beam to pass through a sample 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 measuring system, the structural changes in a cocrystal of syndiotactic polystyrene with triethylene glycol dimethyl ether, were followed during the course of heating.

Small-angle neutron scattering (SANS) is a powerful and convenient method to investigate the higher-order structure of static polymer systems. Owing to technological developments in instruments such as detectors and neutron guides, SANS has extended its presence, even to research concerning time-dependent structural evolution.

The scattering pattern of SANS is determined by the scattering length density (SLD) profile of the object under study, and therefore, it is of great difficulty to derive the sole solution for the arrangement of constituent components from the scattering pattern of SANS. Accordingly, if a system of interest is a multicomponent one, the interpretation of the time-dependent changes in SANS profile is not easy. There are usually several alternatives to explain the variations in the SANS profile, and it is laborious to select an option from them.[1,2]

It is desirable to obtain two or more different kinds of structural information simultaneously from the same sample, which would drastically reduce ambiguities in interpretation. Vibrational spectroscopy has been employed as a complementary tool to X-ray and neutron diffractometry for investigating the structure of polymer systems. Simultaneous analyzes by X-ray scattering and Fourier transform infrared spectroscopy (FTIR) have been developed so far.[3–6] We expect that the combination of SANS with FTIR would also 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.[7,8] Such flexibility of FTIR has been employed also for simultaneous measurement with differential scanning calorimetry (DSC).[9,10]

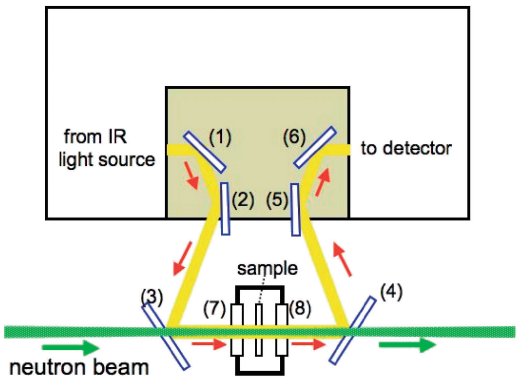

Figure 1. Schematic representation of the simultaneous measurement system. The parts (1)–(6) are mirrors for IR radiation. Mirrors (3) and (4) are designed to reflect only the IR beam and pass the neutron beam. The parts (7) and (8) are sample cell windows.

In this study, we tried to establish the simultaneous SANS/FTIR measurement protocol. For this purpose, a device consisting of a portable FTIR spectrometer and an optical system, which allows a sample to be irradiated with neutron and infrared beams simultaneously, was developed and installed on a small-angle neutron diffractometer. In the proof-of-concept experiment described here, we followed the structural changes on heating a crystalline complex system of syndiotactic polystyrene (sPS) with a low-mass compound.

Figure 1 shows the concept of the simultaneous measurement system, installed at a SANS instrument, KWS2. The system consists of a portable FTIR spectrometer (Perkin-Elmer, Spectrum Two) and an optical system of our own making. Mirrors 3 and 4 in the optical system are Al-coated quartz plates, which transmit neutron beams and reflect infrared rays. With this optical system made up of six mirrors, we can irradiate the sample with the infrared beam coming from the light source of the FTIR spectrometer coaxially with the neutron beam of the SANS diffractometer, filter out the IR beam from the two kinds of transmitted beams, and deliver it to the detector of the spectrometer. For temperature-control measurement, a sample cell is prepared, whose temperature is regulated by circulating oil. It is equipped with two KBr windows of 2 mm thickness on each side, which transmit both the neutron and IR beams. For recording the time-resolved IR spectra and analyzing them, a commercially available software (Perkin-Elmer, Timebase) is employed.

The performance of the simultaneous measurement system was demonstrated with a film sample of the sPS cocrystal with triethylene glycol dimethyl ether (TEGDME). To avoid strong incoherent scattering, fully deuterated syndiotactic polystyrene (d-sPS) ($M_w = 1.1 \times 10^5$ and $M_w/M_n = 1.9$) was synthesized according to the coordination polymerization developed by Ishihara et al.,[11] using fully deuterated styrene with purity more than 98% purchased from Cambridge Isotope Lab. Chloroform of purity 99% and TEGDME of purity 99% were purchased from Sigma-Aldrich and used without further purification. Uniaxially oriented amorphous d-sPS samples about 50-μm thick were prepared by drawing melt-quenched amorphous d-sPS films four times in an oil bath kept at 100 °C. Oriented films of sPS/chloroform cocrystal were obtained by exposing the oriented amorphous films to a vapor of chloroform. sPS/TEGDME cocrystal films were prepared by soaking the sPS/chloroform films to liquid TEGDME for one day and then keeping them in a vacuum oven at 40 °C for an hour. The sample thus prepared forms a δ monoclinic clathrate structure,[12] where TEGDME molecules are encapsulated in the cavities in the crystalline region consisting of sPS helices.[13]

All simultaneous SANS/FTIR experiments were carried out by using the above-mentioned experimental setup installed at KWS2 of the Jülich Centre for Neutron Science (JCNS) outstation at Heinz Maier-Leibnitz Center (MLZ) in Garching, Germany.[14] Scattering data were obtained using a 2D detector with active area of $60 \times 60\,cm^2$ and 128×128 channels. A wavelength $\lambda = 0.7\,nm$ ($\Delta\lambda/\lambda = 20\%$) and a sample-to-detector distance of 4 and 1.35 m were chosen. The typically measured sample area was about $5 \times 5\,mm^2$. The one-dimensional intensity function $I_1(Q)$ was obtained from the corrected 2D data for detector sensitivity, instrumental noise, and scattering from empty cell, by reading pixel values and merging them with a proper width. The data accumulation time for each data point was 15 min. The temperature of the sample cell was controlled with an accuracy of ±0.2 °C. The sample was 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.

It has been confirmed that simultaneous SANS/FTIR measurement can be performed by using the experimental setup described above. Figure 2 represents the changes in SANS 2D images caused by temperature change for a d-sPS/TEGDME cocrystal film. The IR spectral changes measured in parallel with SANS are shown in Figure 3. The starting d-sPS/TEGDME cocrystal showed two intense first-order reflections due to the periodic structure of crystalline lamellae in the meridian direction.[15] The one-dimensional intensity functions, $I_m(Q)$ and $I_e(Q)$, along the meridian and the equator are shown in Figure 4.

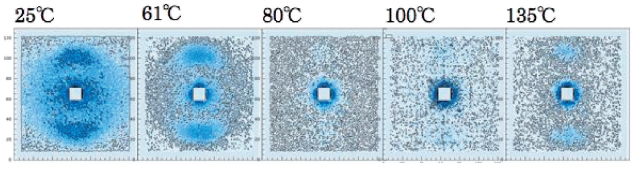

Figure 2. Temperature dependence of SANS 2D images measured on the heating process of sPS/TEGDME cocrystal.

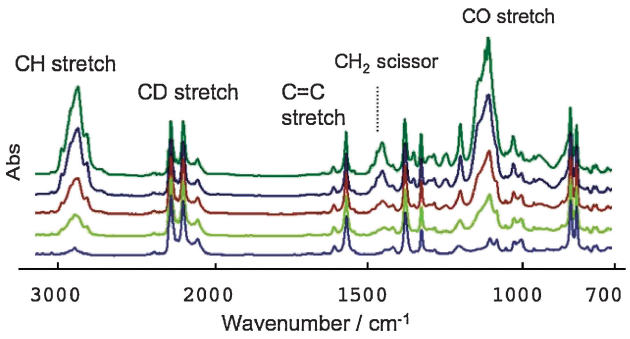

Figure 3. Temperature dependence of FTIR spectra measured in parallel with the SANS measurement in Figure 2 on a sPS/TEGDME cocrystal film. The temperatures are 25, 61, 80, 100, and 135 °C from the top to the bottom.

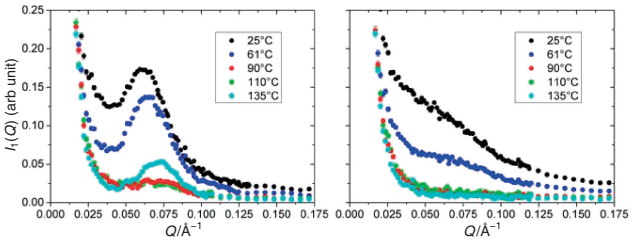

Figure 4. Temperature dependence of SANS one-dimensional intensity functions, $I_m(Q)$ and $I_e(Q)$, along the meridian (top) and the equator (bottom).

The two lamellar reflections are observed clearly up to around 61 °C, and then, they gradually decreases in intensity up to around 80 °C, almost leading to their annihilation. A further increase in temperature brings about the reappearance and a gradual increase in intensity of the two reflections, as shown in Figures 2 and 4. On the contrary, the IR spectra show one-way intensity change. Although the bands due to the vibrational modes of 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, the bands ascribed to TEGDME,[16] such as the C–H stretch around 2874 cm^{-1} and C–O stretch around 1106 cm^{-1} decrease in intensity with an increase in temperature, suggesting that there is no significant change in the d-sPS component. These spectral changes indicate that only TEGDME in the cocrystal film continues to decrease in amount during this heating process, which seems to be reasonable, considering that TEGDME is volatile (bp: 216 °C) because of its relatively low molecular weight of 178.2 $g\,mol^{-1}$.

Under the standard ambient conditions, TEGDME molecules in the sPS cocrystal film are distributed not only in the crystalline region but also in the amorphous region.[13] Since the distribution of TEGDME within the d-sPS matrix is the main cause for the contrast in SLD between amorphous and crystalline regions (ρ_{amor} and ρ_{cryst}), the IR spectral changes suggest that the SANS profile changes can be chiefly ascribed to the changes in distribution of TEGDME, such as migration to the amorphous region and evaporation from the film. By combining the SANS and FTIR information and considering the characteristics of sPS cocrystal and TEGDME, the following structural changes can be

envisaged as a tentative model to explain the SANS profile changes.

Initially, TEGDME having a negative molecular scattering length is included more in the crystalline region than in the amorphous region, which would result in the condition of $\rho_{amor} > \rho_{cryst}$ and the two intense lamellar reflections. In the temperature range from room temperature to around 61 °C, a gradual release of TEGDME molecules would take place mainly from the amorphous region, since TEGDME molecules are less stabilized in the amorphous region, which is consistent with the following two observations in Figure 4. First, the intensities of the lamellar reflection in $I_m(Q)$ does not change much. Second, the background intensity in $I_e(Q)$ clearly decreases. A further increase in temperature up to around 100 °C would induce the migration of TEGDME from the crystalline region to the amorphous region and also the evaporation of TEGDME from the film, since these phenomena are entropically favorable at high temperatures; the higher the temperature, the more TEGDME molecules would migrate from the crystalline region to the amorphous region and subsequently outward. This would cause a strong intensity reduction of the lamellar reflection, since the SLD contrast between the crystalline and amorphous regions becomes lower and approaches the condition of $\rho_{cryst} \approx \rho_{amor}$. A further increase in temperature would bring about the gradual solid-state transition of the crystalline region to the γ phase. Since the unit cell of the γ phase essentially cannot include any guest molecules, the guest molecules are excluded into the amorphous region, as the crystalline region transforms to the γ phase.[17,18] Furthermore, the sPS chains in the crystalline region become packed more tightly in the γ phase, and therefore, the mass density is higher in the γ phase than in the amorphous region. The difference in mass density between the crystalline and amorphous regions increases with an increase in temperature. Since TEGDME and d-sPS have a negative and a positive contribution to SLD, respectively, these two factors, i.e., the migration of TEGDME to the amorphous region and the transformation to a denser lattice, would result in the condition $\rho_{amor} < \rho_{cryst}$, which is consistent with the modest intensity resurgence of the lamellar reflection.

As described above, the present study illustrates the possibility of simultaneous measurement of SANS and FTIR, which is the first SANS experiment of this kind to the best of our knowledge. The IR information obtained in parallel is helpful for interpreting the SANS profile. We expect that the present method would be able to analyze the structure and properties of functional thin films, which have become an important research field due to advances in fabrication technology.[19,20] Although we have employed this prototype system to follow the slow structural changes caused by heating in this study, we believe that this methodology can be applied to time-resolved measurement of second order by improving the FTIR system through redesigning the optical system to gain a high optical throughput and by employing a highly sensitive IR detector, such as MCT detectors. In addition to the simple transmission method that we employed to measure the IR spectra in this study, this system can be combined with other IR measurement techniques like attenuated total reflection (ATR) and reflection absorption spectroscopy (RAS) by modifying the optical system. We consider that the concept of this system would be applicable not only to other neutron scattering methods, such as wide-angle scattering, reflectivity, and grazing incidence SANS, but also to combination with other kinds of spectroscopy, such as Raman and ultraviolet–visible (UV–vis) spectroscopy. We are now planning some improvements in the performance of the IR measurement system as well as an extension of the simultaneous method such as the ones mentioned above.

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References

1 R.-J. Roe, *Methods of X-Ray and Neutron Scattering in Polymer Science*, Oxford University Press, New York, **2000**.
2 J. S. Higgins, H. C. Benoit, *Polymers and Neutron Scattering*, Oxford University Press, New York, **1997**.
3 S. Naylor, W. Bras, G. Derbyshire, G. R. Mant, D. Bogg, A. J. Ryan, *Nucl. Instrum. Methods Phys. Res., Sect. B Res., Sect. B* **1995**, *97*, 253.
4 P. Innocenzi, L. Malfatti, T. Kidchob, S. Costacurta, P. Falcaro, M. Piccinini, A. Marcelli, P. Morini, D. Sali, H. Amenitsch, *J. Phys. Chem. C* **2007**, *111*, 5345.
5 P. J. Ratri, K. Tashiro, *Polym. J.* **2013**, *45*, 1019.
6 K. Tashiro, H. Yamamoto, T. Yoshioka, T. H. Ninh, S. Shimada, T. Nakatani, H. Iwamoto, N. Ohta, H. Masunaga, *Kobunshi Ronbunshu* **2012**, *69*, 213.
7 J. L. Koenig, *Spectroscopy of Polymers*, Elsevior, New York, **1999**.
8 P. R. Griffiths, J. A. de Haseth, *Fourier Transform Infrared Spectrometry*, John Wiley & Sons, New Jersey, **2007**. doi:10.1002/047010631X.
9 F. M. Mirabella, *Appl. Spectrosc.* **1986**, *40*, 417.
10 S. D. Pandita, L. Wang, R. S. Mahendran, V. R. Machavaram, M. S. Irfan, D. Harris, G. F. Fernando, *Thermochim. Acta* **2012**, *543*, 9.
11 N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, *Macromolecules* **1986**, *19*, 2464.
12 Y. Chatani, Y. Shimane, Y. Inoue, T. Inagaki, T. Ishioka, T. Ijitsu, T. Yukinari, *Polymer* **1992**, *33*, 488.
13 F. Kaneko, K. Sasaki, *Macromol. Rapid Commun.* **2011**, *32*, 988.
14 A. Radulescu, V. Pipich, A. Ioffe, *Nucl. Instrum. Methods Phys. Res., Sect. A*, **2012**, *689*, 1.
15 F. Kaneko, N. Seto, K. Sasaki, S. Sakurai, T. Kimura, *Macromol. Chem. Phys.* **2013**, *214*, 1893.
16 H. Matsuura, T. Miyazawa, K. Machida, *Spectrochim. Acta, Part A* **1973**, *29*, 771.
17 G. Guerra, V. M. Vitagliano, C. De Rosa, V. Petraccone, P. Corradini, *Macromolecules* **1990**, *23*, 1539.
18 F. de Candia, M. Carotenuto, L. Guadagno, V. Vittoria, *J. Macromol. Sci., Part B: Phys.* **1996**, *35*, 265.
19 K. Ariga, Y. Yamauchi, G. Rydzek, Q. Ji, Y. Yonamine, K. C.-W. Wu, J. P. Hill, *Chem. Lett.* **2014**, *23*, 36.
20 Y. Shimakawa, *Bull. Chem. Soc. Jpn.* **2013**, *86*, 299.

