Application of Simultaneous Measurement System Combining Wide *Q*-Range Small-Angle Neutron Scattering and Polarized Fourier Transform Infrared Spectroscopy: Cocrystal of Syndiotactic Polystyrene with Methyl Benzoate

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We recently developed a simultaneous measurement system combining a wide *Q*-range SANS instrument and a Fourier-transform infrared (FTIR) spectrometer equipped with an infrared polarizer. The information obtained by high *Q* neutron scattering and polarized FTIR spectroscopy helps to increase the reliability of structural analysis by SANS on complicated systems. In this study, we applied this simultaneous measurement system to a cocrystal system of syndiotctic polystyrene (sPS) and methyl benzoate (MeBA). The neutron scattering provided the evidence that MeBA molecules were certainly incorporated into the crystalline region of sPS. The polarized FTIR measurements showed that the guest MeBA has a certain orientation against the sPS lattice. With the help of different kinds of structure information, the thermal behavior of sPS/MeBA cocrystal was able to be analyzed in detail.

KEYWORDS: cocrystal, syndiotactic polystyrene (sPS), small angle neutron scattering (SANS), wide angle neutron scattering (WANS), wide-Q range measurements

1. Introduction

Small angle neutron scattering (SANS) has been employed as a powerful tool for higher order structural analyses for a variety of polymer systems ranging from solutions and gels to solid states. However, since the SANS profile is solely determined by the scattering length density (SLD) contrast, the analysis of SANS profile is a hard task. The interpretation in the SANS profile becomes more difficult as the system to be studied becomes more complex. Therefore, on the application of small angle neutron scattering (SANS) to a complex multi-component system, it is desirable to obtain two or more different kinds of structural information simultaneously from the same sample in order to improve the reliability of analyses. For this purpose, Fourier transform infrared (FTIR) spectroscopy is a strong candidate, which is able to provide a variety of molecular-level structural information such as molecular conformation, orientation and intermolecular interactions.

For this purpose, we developed a simultaneous SANS/FTIR measuring system and applied it to polymer solid states several years ago [1-2]. To collect more structural information, we have recently introduced this methodology to a time-of-flight small and wide angle neutron scattering instrument (TAIKAN at J-PARC MLF, JAPAN), covering up to a wide angle neutron scattering (WANS) range on one measurement [3]. In addition, a remote control polarizer system was also installed for polarization analysis of IR bands, as shown in Fig. 1. The present system has the following advantages for the research on polymer material. First, the hierarchical structures in polymer materials are accessible at the same time; SANS provides the information about the higher order structures, such as lamellar structures, and WANS provides the information about the crystal lattice. Second, the spatial arrangement of chemical groups is reflected in polarized IR spectra when suitably oriented specimens are available.

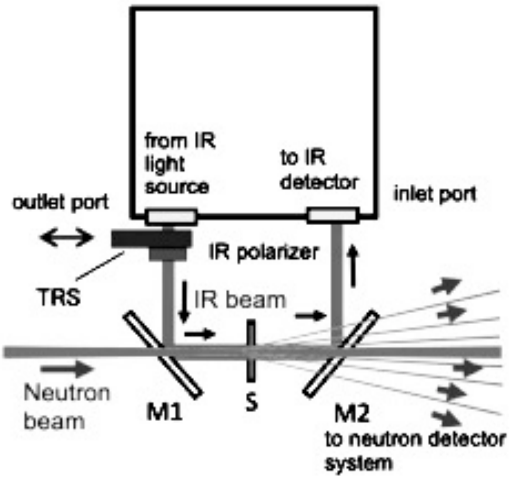

Fig. 1. An experimental setup for simultaneous measurement of wide-*Q* small angle neutron scattering and polarized FTIR spectroscopy, which is installed at the TAIKAN diffractometer at BL15 in J-PARC MLF. M1 and M2 are aluminum coated quartz mirrors and TRS is a translational and rotational stage system.

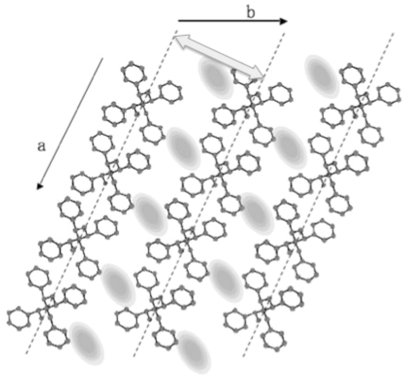

Fig. 2. A schematic representation of sPS coccrystal (monoclinic δ clathrate). sPS helices are aligned along the *a*-axis into polymer sheets, between which guest molecules are sandwiched. The grey eclipses are the spaces where the guest molecules are located. The two-direction arrow represents the repeat period of the 010 direction.

In order to check the performance of this system, we have applied this measurement system to cocrystals of syndiotactic polystyrene (sPS). sPS is a crystalline polymer having unique characteristics; it exhibits a variety of crystalline states, depending on crystallization conditions and subsequent treatments [4], and furthermore, it forms cocrystals with a variety of chemical compounds. The crystalline region of sPS cocrystal consists of a porous host lattice and guest molecules; host sPS chains taking $(T_2G_2)_2$ helical conformation are aligned forming polymer sheets, between which guest molecules are stored, as shown in Fig. 2.

In this paper, we report the characteristics of sPS cocrystal containing methyl benzoate (MeBA), featuring the temperature dependent changes in neutron scattering profiles and polarized FTIR spectra obtained by this simultaneous measurement system.

2. Experimental

2.1 Sample

sPS cocrystal films for neutron scattering measurements were prepared by the following procedure. Fully deuterated sPS (d-sPS) (weight average molecular weight: 2.3×10^5) was synthesized through the coordination polymerization using a rare earth catalyst from fully deuterated styrene with an isotopic purity of 98% [5]. Uniaxially oriented amorphous d-sPS films, about 50 μm thick, were prepared by quenching a melt of d-sPS in an ice–water bath, drawing the melt-quenched film four times at 373 K, and clipping well oriented portions from the drawn films. d-sPS cocrystal films containing toluene as guest (d-sPS/h-toluene) were obtained by exposing the oriented amorphous films to a vapor of toluene. To obtain d-sPS cocrystal containing MeBA (d-sPS/h-MeBA), d-sPS/h-toluene films were subjected to the plasticizer assisted guest exchange procedure [6], in which deuterated chloroform ($CDCl_3$) was used as a plasticizer. These films were kept in a vacuum drier at 40 °C for 1 hour before measurements. Organic solvents, toluene with purity of 99% purchased from Nacalai Tesque (Kyoto, Japan) and $CDCl_3$ purchased from Acros Organics (Waltham, US) were used without further purification. MeBA with purity of 99% was purchased from Tokyo Chemical Industry (Tokyo, Japan) and used without further purification.

2.2 Measurements

Wide-Q range observation of neutron scattering measurements were performed using installed on the BL15 beamline at J-PARC, Tokai, Japan [7]. By using large-area detector banks and white neutron beams in the wavelength (λ) range of $\lambda \sim 0.7$–8 Å together with the time-of-flight method, TAIKAN simultaneously covers a wide Q range from 5×10^{-3} to 15 $Å^{-1}$, where the magnitude of the scattering vector Q is defined as $Q = 4\pi\sin(\theta/2)/\lambda$ (where θ represents the scattering angle). However, the observed Q range in the present study was limited to $8 \times 10^{-3} \cdot Å^{-1} < Q < 1\ Å^{-1}$ owing to incoherent scattering from hydrogen atoms in higher Q range ($Q > 1\ Å^{-1}$).

For polarized FTIR measurements, an FTIR spectrometer (JASCO, VIR-200) equipped with an MCT detector was employed together with an IR polarizer mounted on a combination of remote controlled rotary and translational stages (Sigma Koki).

3. Results and Discussion

Fig. 3 shows the temperature dependence of the two-dimensional (2D)-SANS profiles for a one-dimensionally oriented d-sPS/MeBA cocrystal film observed using the TAIKAN instrument. The 2D-SANS profile provides the information about not only higher-order structures but also the interior of the cocrystal lattice, owing to the characteristic of TAIKAN covering a wide-Q range simultaneously. d-sPS/MeBA cocrystal exhibits two types of reflections, that is, lamellar reflections (LRs) on the meridian of the SANS region (approximately $Q_y = 0.06$ Å^{-1}) and two 010 reflections on the equator of the high-Q region (approximately $Q_x = 0.58$ Å^{-1}). These two kinds of reflections exhibit different temperature dependence during the course of heating from 25°C to 125°C.

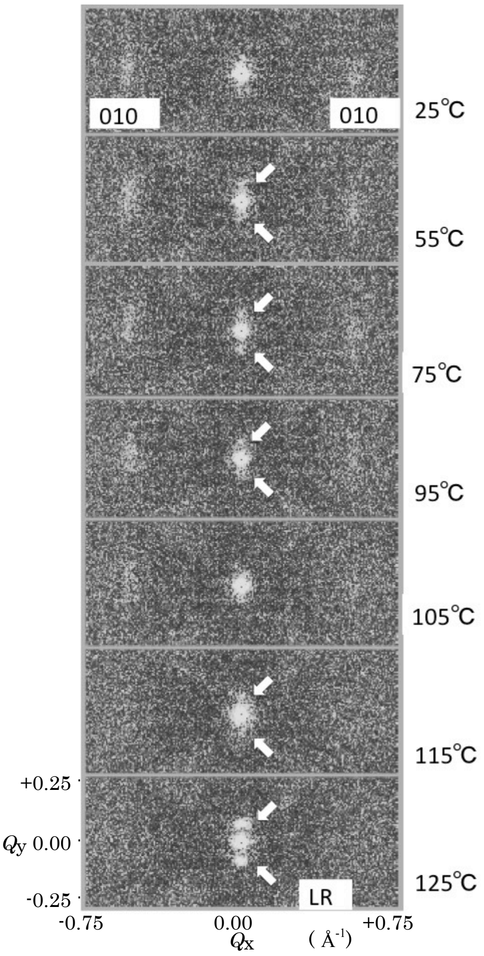

Fig. 3. Temperature dependent SANS profile changes of a one-dimensionally oriented film of sPS/MeBA cocrystal. The Q_x and Q_y directions are parallel to the horizontal and vertical axes. The white arrows indicate the lamellar reflections.

The 010 reflections clearly appear from room temperature up to around 95°C, and then they gradually wane as the temperature decreases. Finally, they disappear at 125°C. On the other hand, the LRs show more complicated temperature changes. They are not clearly observable at 25°C, but they become observable in the elevated temperature range between 55°C and 75°C. A further temperature rise makes them weakened, and they almost disappear around 105°C. However, they regain intensity with further temperature increase and appear clearly at 125°C. The distribution of protonated guest molecules in the d-sPS cocrystal film is the principal factor to determine the intensities of these two types of reflections.

The 010 reflections are directly associated with the guest inside the cocrystal lattice because the 010 plane corresponds to the repeat distance of the guest molecules as shown in Fig. 2. The scattering length density (SLD) contrast between protonated guest molecules and surrounding fully deuterated sPS matrix causes the 010 reflections. Accordingly, the observed temperature dependence of the 010 reflections indicates that MeBA molecules are certainly included in the d-sPS cocrystal lattice as guests at 25 °C but they are gradually released from the crystalline region in the elevated temperature range, which is consistent with the temperature dependence of polarized FTIR spectra observed simultaneously, as described below.

Fig. 4 reproduces the temperature dependent changes of C-H stretch region, to which guest MeBA molecules dominantly contribute. The bands in the 3070-3030 cm^{-1} are assigned to the aromatic ring modes. The three bands at 3000, 2950, and 2900 cm^{-1} are due to the methyl group; the first and second bands are assigned to the out-of-plane and in-plane antisymmetric C-H stretch modes, $\nu_{as}(CH_3)$, and the third one is assigned to the symmetric C-H stretch mode, $\nu_s(CH_3)$. At 25°C, these bands exhibit clear polarization in this 3100–2800 cm^{-1} region suggesting that molecules are kept oriented in the crystalline region. The aromatic-ring bands, in-plane $\nu_{as}(CH_3)$ band and $\nu_s(CH_3)$ band are observed larger with IR radiation polarized perpendicular to the drawing direction of the cocrystal film, which is the same feature observed in d-sPS/toluene cocrystal [3]. Accordingly, it is indicated that the aromatic ring plane of MeBA is set nearly perpendicular to the *c*-axis of the host sPS lattice. During the heating process, these bands of MeBA gradually decrease in intensity, in particular, their intensity changes are obvious above 100°C. As can been seen, these bands come close to anihilation at 125°C, suggesting that most guest MeBA molecules are released from the sPS cocrystal lattice. It is also suggested that MeBA molecules are given off to the outside of the film when released from the crystalline region at high temperature.

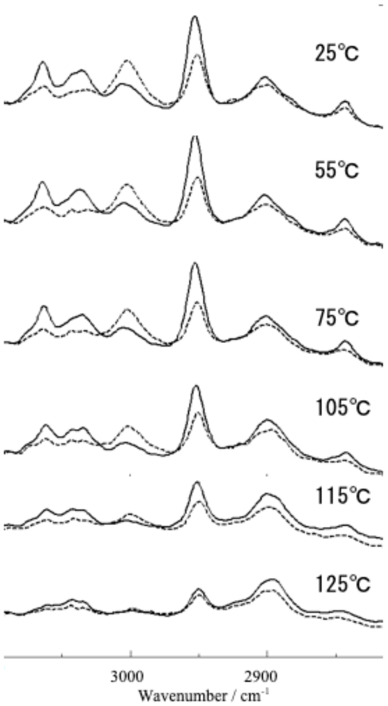

Fig. 4. Temperature dependent changes in polarized FTIR spectra (in absorbance) of a uniaxially drawn sPS/MeBA cocrystal film on heating process. Solid and broken lines represent the spectra measured with IR radiation polarized perpendicular and parallel to the drawing direction of the film sample.

On the contrary, the LRs are caused by the SLD contrast between the amorphous and crystalline regions of sPS cocrystal. Accordingly, the weak LRs are not necessarily related to the absence of guest molecules in the crystalline region. The weak intensity only suggests that the SLD contrast is low, regardless of the guest concentration in the crystalline region.

The complicated temperature dependence of the LRs can be attributed to the two factors; one is the difference in the volatility of the guest MeBA between in the amorphous region and in the crystalline region, and the other is the transformation of the cocrystal lattice. The volatility of small guest molecule increases with temperature. The volatility is higher in the amorphous region than in the crystalline region. Accordingly, on heating the elimination of MeBA starts in the amorphous region, and then it shifts to the crystalline region.

The slight intensity increase of the LRs in the range of 25°C to 75°C can be ascribed to an increase in SLD due to the elimination of MeBA from the amorphous region. Polarized FTIR spectra show a slight increase in dichroic ratio for the in-plane

$\nu_{as}(CH_3)$ band at 2950 cm^{-1}, which is attributable to a preferential decrease in the MeBA concentration in the amorphous region. The subsequent intensity decrease observed in the higher temperature range can be attributed to the guest elimination from the crystalline region, which is consistent with the observed IR spectral changes that all the bands due to MeBA continuously decrease in intensity.

At the highest temperature 125°C, the LRs clearly regain their intensity, whereas the IR bands of MeBA continue to decrease in intensity up to this temperature. The guest is close to extinction in both the amorphous and crystalline regions of the sample film. The recovery of the LRs, therefore, is not attributable to the distribution of MeBA. At elevated temperature, the sPS cocrystal gradually transforms to a crystal modification called γ, releasing the guest to the amorphous region. The cavities in the crystalline region shrink during the transformation to γ, which makes the density of the crystalline region higher than that of the amorphous region. Therefore, the larger portion of the sPS cocrystal lattice transforms to γ, the higher SLD contrast is generated between the amorphous and crystalline regions, which well accounts for why the LRs regain their intensity on heating from 105 to 125˚C.

As described above, the information obtained by polarized FTIR spectra measured in parallel with SANS profiles is quite helpful for interpreting what is the principal cause for the changes in SANS profile. Furthermore, the extension of Q range up to WANS region has enriched structural information of crystalline polymers; it allows us to see what happens inside of crystalline lamellae.

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