Structural study on the molecular conformation and orientation of large molecules stored in the cocrystals of syndiotactic polystyrene using simultaneous SANS, WANS and polarized FTIR measurements.

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1. Introduction

Syndiotactic polystyrene (sPS) exhibits a variety of solid states. One of the important characteristics of sPS is the formation of crystalline cocrystals, where organic compounds are stored as guests in the cavities in the crystalline region. The guest molecule can be exchanged with other molecule; we have clarified that a variety of compounds including functional molecules can be incorporated into sPS lattice by using this guest exchange phenomenon [1, 2]. The sPS cocrystals seems to have a significant potential as a new kind of functional material [3-5]. Actually, it has been clarified from the scattering (X-ray and neutron) and FTIR experiments that sPS forms cocrystals with polymeric materials, such as, polyethylene glycols[6,7]. Since the volume of this kind of guest molecules is much larger than the available space in a cavity of sPS cocrystals, it is inferred that such a long guest molecule is accommodated in a completely different manner from the ordinary sPS cocrystal, where one guest molecule occupies a cavity. It is highly plausible that the long molecule settles in the sPS cocrystal by using several cavities.

The purpose of this study is to clarify the structure and orientation of such large guest molecules stored in the cocrystals of sPS. So far, we have been studying sPS cocrystals by using IR spectroscopy, X-ray scattering and also neutron scattering [8]. Furthermore, we have recently developed a simultaneous time-resolved SANS/FTIR measuring system [9,10], which is able to supply the information about not only higher-order structure but also the molecular-level structure and the amount of chemical species. To enrich structure information, we have tried to introduce this methodology to a small- and wide-angle neutron scattering instrument, BL15 TAIKAN, and also analyze the polarization of vibrational modes by installing a polarizer.

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2. Experiment

For this study, we built an experimental setup shown in Figure 1 for simultaneous neutron scattering and polarized FTIR measurements, as shown in Figure 1. For polarization analyses, a remote control IR polarizer was set just after the outlet IR beam port of a portable FTIR spectrometer (JASCO, VIR200). The two mirrors are Al-coated quartz plates, which transmit neutron beams and reflect infrared rays. The first mirror acts as a beam mixer and the second one as a beam separator. The IR and neutron beams impinges the same position of the sample coaxially and the transmitted beams are delivered to their own detectors.

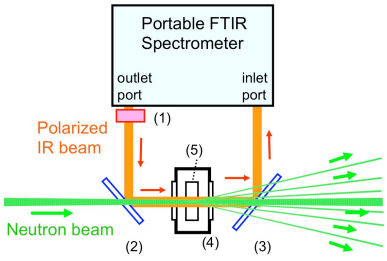

Figure 1: Simultaneous SANS/WANS/ Polarized FTIR measuring system; (1) polarizer, (2) (3) mirrors, (4) cell housing and (5) sample cell.

Fully deuterated syndiotactic polystyrene (d-sPS) was synthesized. Uniaxially oriented amorphous d-sPS samples, about 50 μm thick, were prepared by quenching a melt of d-sPS into an ice–water bath, drawing the melt-quenched film four times in an oil bath kept at 100˚C, and clipping well oriented portions from the drawn film. The oriented amorphous films were exposed to a vapor of toluene to give oriented samples of d-sPS/toluene cocrystal. The cocrystal films were soaked in a target guest molecule/deuterated chloroform mixture over a week and then kept in a vacuum oven at 40˚C for an hour to remove excess chloroform, giving uniaxially oriented cocrystal film samples.

Thus prepared d-sPS cocrystal film samples were subjected to simultaneous SANS/WANS/FTIR measurements. Temperature dependent changes were observed in the range of 25 to 125˚C.

3. Results

Figure 2 shows an example of temperature dependent SANS and WANS profile changes. The fiber axis direction is set parallel to the vertical direction, and therefore, the reflections due to lamellar stacking appear on the meridian. The d-sPS cocrystal includes diethylene glycol dibenzoate (DEGDBA), $C_6H_5O(C_2H_4O)\ C_6H_5$, as guest. In such d-sPS cocrystals containing protonated guests, the distribution of the guest is the principal factor to determine the neutron scattering profile.

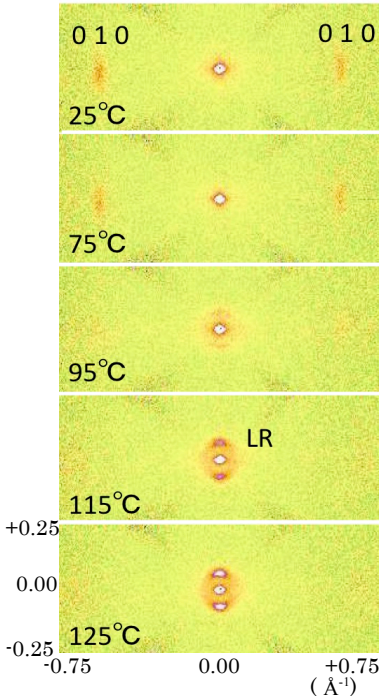

Figure 2. Scattering profile of a uniaxially oriented film of d-sPS / h-DEGDBA cocrystal. LR: lamellar reflection.

In the lower temperature region, the sPS cocrystal showed clear 010 reflections at around q = 0.6 $Å^{-1}$ on the equator, which indicated that DEGDBA molecules were stored in the crystalline region; the regular arranagement of DEGDBA in the lattice creates a clear scattering contrast. However, the 010 reflections gradually waned as the temperature increased. Instead the lamellar reflections appeared on the meridian and increased in intensity with temperature.

These changes in the WANS and SANS regions suggest the migration of protonated guest DEGDBA molecules from the crystalline region to the amorphous region of deuterated sPS matrix, since the migration results in a decrease in the scattering contrast (SC) within the crystal lattice and an increase in the SC between the crystal lattice and amorphous regions.

The polarized IR spectra obtained were consistent with this interpretation. The host d-sPS did not show any significant spectral changes, keeping the polarization of each band, which suggests that the orientation and conformation of d-sPS remained almost unchanged during heating process. The bands due to DEGDBA did not show significant intensity changes, which suggests that the gross amount of DEGDBA within the film sample was kept unchanged.

4. Conclusion

As described above, the present study has shown that the simultaneous SANS, WANS and FTIR measurements are able to provide valuable information about the polymer co-crystal system. By combining the data obtained by SANS with those obtained by WANS, the location of guest molecules can be derived with a larger certainty. Furthermore, the polarized IR spectroscopy can add the information about the conformation and orientation of the host and guest.