

Guest Exchange Behavior of Syndiotactic Polystyrene with Crown Ethers

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1 Introduction

One of the important properties concerning the solid states of sPS is the variety of crystalline states. It shows several polymorphs depending on the crystallization conditions and subsequent treatments. Also, it forms some co-crystal states with a variety of chemical compounds. The co-crystal states of sPS are classified into at least four groups, depending on the crystal system and the size and shape of spaces that guest molecules occupy. In these co-crystal states, guest molecules are included in cavities formed by sPS helices of TTGG conformation. The polymer-crystalline-region-based complex found in sPS is unprecedented in synthetic polymers with respect to considerable variety of guest molecules. The potential of sPS co-crystal states as new kinds of functional polymer materials attracts attention, and many studies are actively being carried out.

A striking property of sPS co-crystals is that the guest molecules can be replaced smoothly when exposed to a vapor or a liquid of the substitute. This guest exchange phenomenon gives an advantage to sPS of forming crystalline complexes even with chemical compounds that are difficult to incorporate into the crystalline region by the solution-cast and solvent-induced crystallization. Furthermore, the addition of an additive into the substitute significantly promotes the guest exchange process of sPS complexes. However, the details of the role of additives remain hidden from view.

To tackle this issue, we tried to follow the guest exchange process under the influence of additives by simultaneous WAXS and SAXS measurements.

2 Experiment

sPS was provided by Idemitsu Bussan Corp. Three crown ethers, 12-crown-4, 15-crown-5, and 18-crown-6 were purchased from Sigma-Aldrich and used as new guests without further purification. Acetone purchased from Nacalai esque was used as additive. In order to measure clear lamellar reflections in a well defined area, 4-5 times uniaxially drawn sPS films about 50 μm thick were prepared. Starting samples of sPS/chloroform cocrystal were prepared by exposing the films to chloroform vapor. Time resolved SAXS and WAXS measurements were carried out at BL-6A and BL 9C.

The guest exchange process was initiated by injecting a mixture of new guest and acetone into a glass capillary containing several pieces of sPS/chloroform complex film.

3 Results and Discussion

It has been found that acetone acts as a quite effective promoter for the guest exchange process of sPS co-

crystals with crown ethers. On the exposure of sPS/chloroform films to a neat liquid of crown ethers, no marked changes appeared both in the SAXS and WAXS images at least for several hours. However, when a mixture of crown ether and acetone at a suitable ratio, e.g. 1:1 volume ratio, was applied to the film, various changes were observed. Fig. 1 shows the changes in SAXS and WAXS images during the guest exchange by exposing to a 1:1 volume ratio 15-crown-5/acetone mixture. In the SAXS region, the reflections due to the lamellar repeat distance showed a gradual shift to a lower angle after the inception of the guest exchange procedure, which indicates that the lamellar spacings are expanded during the course of the guest exchange. Meanwhile, there appeared some intensity changes in certain reflections reflecting cocrystal structures. The intensity change of the 010 reflection indicated by the red arrow, which is very sensitive to the repeat structure of polymer layer and guest layer, suggests that old guest chloroform had been replaced with new guest 15-crown-5 during this period. The replacement has been confirmed also by FTIR spectroscopy. In addition to this intensity change, the 110 reflection due to the ϵ -clathrate co-crystal appeared at the blue arrowed point.

As described above, these observations by time-resolved SAXS/WAXS measurements have pointed out that the guest exchange proceeds smoothly in the δ clathrate phase under the influence of acetone, accompanied with the generation of ϵ clathrate.

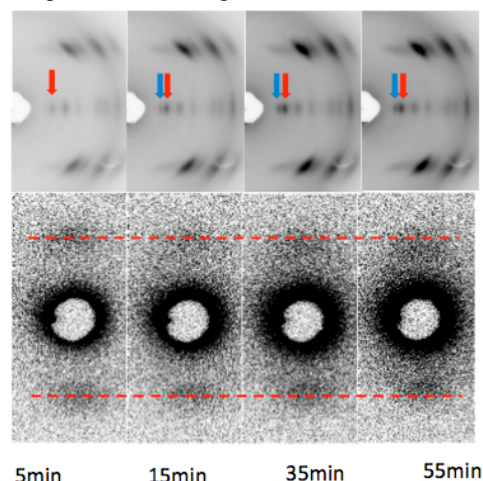


Fig. 1 Changes in WAXS (top) and SAXS (bottom) images during the guest exchange process of sPS/chloroform co-crystal with a 1:1 volume mixture of 15-crown-5 and acetone.

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