BL-6A&BL-10C/2014G570

SWAX measurement on co-crystallization of syndiotactic polystyrene with linear polymers

Fumitoshi Kaneko[1,*] and Shuma Sato[1]
[1]Graduate School of Science, Osaka University, Toyonaka 560-0043, Japan

1 Introduction

Syndiotactic Polystyrene (sPS) occupies a peculiar position among crystalline synthetic polymers. 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 of sPS co-crystal states as new kinds of functional polymer materials attracts attention, and many studies are actively being carried out.

Recently we have clarified that cyclic and linear molecules consisting of ethylene oxide (CH_2CH_2O) repeat units can be easily incorporated into the crystalline region of sPS co-crystals through guest exchange procedure. Chemical compounds with a wide variety of molecular weights, from 176 (12-crown-4) to 2000 (PEG 2000), have been confirmed to form co-crystal with sPS.

We have expected that other polymeric compounds would also exhibit complexation with sPS, if the following prerequisites are satisfied; (1) a strong affinity to the cavity in host sPS crystalline region and (2) a suitable flexibility of the main chain. According to this expectation, we have studied the complexation of polypropylene glycol (PPG) [$(\text{-}CH_2CH(CH_3)O\text{-})_n$] oligomers with sPS in this study.

2 Experiment

sPS was provided by Idemitsu Kosan Corp. The following PPG related compounds were employed as new guests: dipropylene glycol dimethyl ether (DPGDME), Tripropylene glycol (TPG), and PPGs with mw 400 and 1000 (PPG400 and PPG1000). Diethylene glycol dimethyl ether (DEGDME) was also used for comparison.

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 sPS films to chloroform vapor. Time resolved simultaneous SAXS and WAXS measurements were carried out at BL-6A and BL-10C. The guest exchange process was initiated by injecting a liquid of new guest (or a mixture with an additive) into a glass capillary containing several pieces of sPS/chloroform co-crystal film.

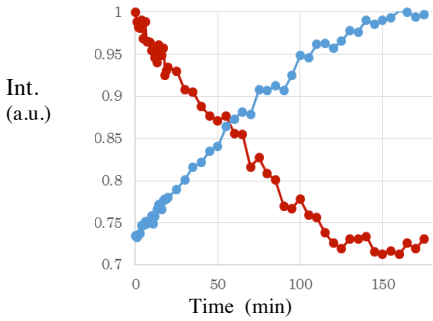

Fig. 1. Intensity changes in 010 (blue) and $\bar{2}10$ (red) reflections during the guest exchange process from chloroform to DPGDME.

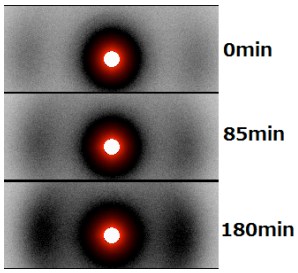

Fig. 2. SAXS profile changes during the guest exchange process of sPS co-crystals. The two spots are due to the lamellar stacking of sPS co-crystals.

3. Results and Discussion

On exposure of sPS/chloroform films to a neat liquid of DPGDME, marked changes appeared both in the SAXS and WAXS images. Fig. 1 shows the intensity changes in the 010 and $\bar{2}10$ reflections on the equator in the WAXS image, which kept on changing over 2 hours. In the meantime, the lamellar reflections in the SAXS images increased significantly in intensity and shifted to a lower angle. These changes indicate that DPGDME is also able to form a co-crystal structure with sPS. Compared with the guest exchange process of DEGDME, in which major SAXS and WAXS changes completed in about 10 min, DPGDME spends a considerable amount of time intruding into the sPS co-crystal lattice, which is presumably due to the steric hindrance of side methyl groups.

We also investigated the changes in SAXS and WAXS profiles of sPS co-crystal films after the guest exchange treatment for about a week, and observed similar changes, which strongly suggests the possibility that sPS forms co-crystals with high-molecular PPGs.

* toshi@chem.sci.osaka-u.ac.jp