

SWAXS Study on Co-crystallization of Syndiotactic Polystyrene with Some Linear Molecules

Fumitoshi Kaneko^{1,*} and Shuma Sato²

¹Graduate School of Science, Osaka Univ., 1-1 Machikaneyama, Toyonaka Osaka, 560-0044, Japan

1 Introduction

Syndiotactic polystyrene (sPS) occupies a unique position among synthetic polymer materials.[1-2] Contrary to commonly used atactic polystyrene (aPS), sPS is a crystalline polymer that exhibits complex polymorphism. Depending on crystallization conditions and subsequent treatments, a variety of crystalline modifications appear. Besides, sPS forms cocrystal structures with many different chemical species. It has been found that sPS forms at least four kinds of cocrystal structures. Fig. 1 shows the monoclinic δ clathrate structure, which is most commonly observed.[3] The sPS helices taking trans-trans-gauche-gauche (TTGG) conformation are aligned in a line forming polymer sheets. The guest molecules are included in the cavies generated between the neighboring polymer sheets.

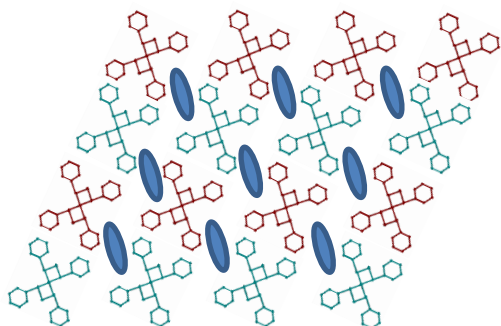


Fig. 1: Monoclinic δ clathrate cocrystal of sPS.

The guest molecules in the sPS cocrystal can be substituted by exposing to a vapor, liquid, and solution of other chemical. By using this guest exchange phenomenon, we make sPS cocrystals with a variety of chemicals that cannot be introduced as guests directly by the ordinary preparation methods, such as solution crystallization and solvent induced crystallization. In particular, the mixing of an additive into the new guest molecule significantly promotes the guest exchange process in sPS cocrystals. Recently, it has been found that even long polymeric molecules having ethylene oxide repeat units ($-\text{C}_2\text{H}_4\text{O}-$) can be introduced into sPS cocrystals by using this additive assisted guest exchange method.[4] Cocrystallization with polyethylene glycols with molecular weight of 2000 has been confirmed.[5]

In this study, we have investigated the structural changes during the additive assisted guest exchange process, in particular, with regard to the following two points. One is the behavior and promotion effect of some additives and the other is the possibility of cocrystallization of sPS with other polymeric compounds.

2 Experiment

sPS was provided by Idemitsu Kosan Corp. The weight-average molecular weight \bar{M}_w was 179k and the polydispersity index \bar{M}_w/\bar{M}_n was 3.08. In order to measure clear lamellar reflections in a well defined area, uniaxially oriented sPS/chloroform samples about 50 μm thick were prepared by drawing melt quench sPS glass films four times and then exposing a vapor of chloroform. Starting samples of sPS/chloroform thus prepared were subjected to the measurements on the guest change process.

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 mixture of new guest with an additive into a glass capillary containing several pieces of sPS/ chloroform cocrystal film. IR spectral measurements were carried out by using a Perkin-Elmer Spectrum Two spectrometer.

For the study on the additive effect, three different chemicals, acetone, tetrahydrofuran (THF) and acetonitrile (AN), were employed as additives and polyethylene glycol dimethyl ether with molecular weight of 500 (PEGDME500) as a new guest. Cocrystallization of sPS with polypropyleneglycols with molecular weight of 400 and 1000 (PPG400 and PPG1000) were carried out by using acetone as additive.

3 Results and Discussion

3.1 Influence of Additives

When acetone and THF were employed as additives, the low-angle shifts of crystalline lamellar reflections were observed in the initial process of the guest exchange process, irrespective of the concentration of the additive, as shown Fig. 2. In particular, the shift was completed very quickly within 1 min for THF. The repeat period of lamellae change from 100Å to 116Å for acetone and to 113Å for THF. On the other hand, no particular low angle shifts were not observed for AN.

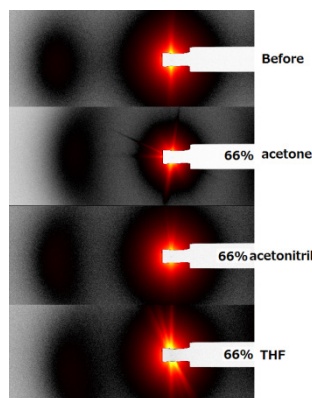


Fig. 2: SAXS profile changes during the guest exchange process of sPS co-crystals. The two spots are due to the lamellar stacking of sPS co-crystals.

According to the results of IR measurement, the TTGG conformation of sPS remained unchanged during the guest exchange process, which indicates the crystalline lamellae were kept. It follows that the low-angle shift of the lamellar reflections was caused by the swelling of the amorphous region of the starting sPS/chloroform cocrystal.

The difference in the swelling behavior between AN and the others is attributable to the affinity between solvents and host polymer matrix. The solubility parameter of polystyrene is 9.0, whereas those of acetone, THF and AN are 9.9, 9.1 and 11.9, respectively. Accordingly, it can be considered that AN does not swell the amorphous region because of its low affinity to sPS amorphous region. It seems that the swelling caused by acetone and THF promotes the diffusion of the new guest molecule in the amorphous region before its intrusion into its amorphous region.

The WAXS profile of sPS cocrystal systems reflects the structural change within crystal lamellae. Some reflections appearing on the equator of the fiber diagram of sPS cocrystal, such as 010 and $\bar{2}$ 10 reflections, can be used as the indicators how the guest exchange from the original guest chloroform to the new guest PEGDME500 proceeds. The intensity changes in these reflections completed within 1 hour, when acetone was mixed with PEGDME500 at the volume ratio of 2:1. On the other hand, the intensity change proceeded gradually for THF and AN. Even after 2.5 hours from the inception, the intensity change was in progress. In particular, it went quite slow for AN, which would be related to the lack of the swelling in the amorphous region.

The difference observed in WAXS between acetone and THF suggests that the acceleration effect of additives on the guest exchange process is not determined only by the diffusibility of new guest molecules in the amorphous region. Our previous study showed that the additive penetrates into the crystalline region and takes the place of the original guest and then the new guest is gradually replaced with the additive. Accordingly, the replacement from the additive to the new guest would not proceed smoothly, if the affinity between the additive and the cavity of sPS is considerably high. We infer that the strong affinity of THF to sPS host would retard the intrusion of new guest PEGDME500.

3.2 Cocrystallization of sPS with PPG400 and PPG1000

So far, we have already confirmed that sPS forms cocrystals with dipropylene glycol dimethyl ether (DPGDME) as well as diethylene glycol dimethyl ether (DEGDME), though the cocrystallization with DPGDME proceeds rather slower than that with DEGDME. It is strongly suggested that polymeric compounds consisting repeat units of $(-\text{CH}_2\text{CHCH}_2\text{O}-)$ can be incorporated into sPS lattice just like polyethylene glycols.

The IR spectra of sPS cocrystal films, which had contained chloroform as the original guest and were subjected to the guest exchange treatment with solutions of PPG400 and PPG1000, are reproduced in Fig. 3. The 1219 cm^{-1} band due to chloroform disappeared and the characteristics of PPGs, such as a strong and broad band

around 1100 cm^{-1} , appeared in the resultant films for both cases.

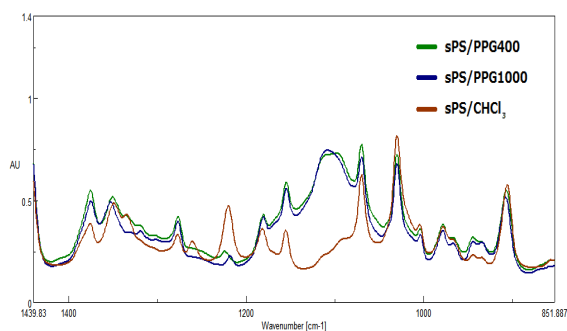


Fig. 3: IR spectra of sPS cocrystals with original guest chloroform and new guests PPG400 and PPG1000.

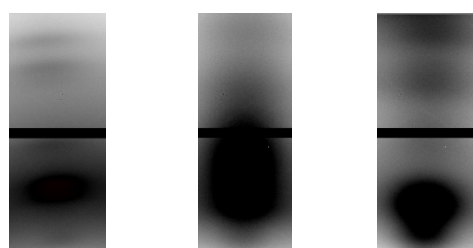


Fig. 4: WAXS diffraction profiles along the equator for drawn sPS cocrystal films containing chloroform (left), PPG400 (middle) and PPG1000 (right).

The formation of cocrystal was also confirmed by WAXS profile, as shown in Fig. 4. The profile significantly changed during the guest exchange treatment both for PPG400 and PPG1000, suggesting the uptake of these new guest molecules. However, there was a large difference between PPG400 and PPG1000. There is a possibility that the packing mode of PPGs in sPS cocrystals varies depending on their chain length.

References

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