

Structural Analysis of Crystalline Polymeric Membrane

Shigeru OKAMOTO*, Masayoshi SUZUKI, Yusuke YAMAMOTO,
Hiroaki YOSHIMIZU and Yoshiharu TSUJITA
Nagoya Institute of Technology, Nagoya, 466-8555, Japan

Introduction

It is well known that syndiotactic polystyrene (sPS) in semi crystalline shows four polymorphic forms, i.e., α , β , γ and δ [1,2]. The α and β forms contain planar zigzag chains having T4 all-trans conformation, while the γ and δ forms contains T2G2 helical conformation. The δ form has a clathrate structure with small molecules accommodated in the crystalline structure. It has been reported that δ form can be transformed into γ form by heating above its glass transition temperature, and into α form by heating at higher temperature. However, the mechanism has not been well investigated so far. In this study, we focused on the transitions from δ to γ and to α -form by thermal stimuli. The structural changes during heating or isothermal annealing in a sPS/ solvent complex were studied in situ by the time-resolved small- (SAXS) and wide-angle (WAXS) X-ray scattering techniques (TR-SWAXS), using a synchrotron radiation facility. Recently δ -form has been also reported to transform into δ_c -form by soaking it in acetone and successively in methanol, where δ_c -form has molecular-size cavities by removal of solvent molecules. It is also interesting to investigate whether or not this δ_c -form exists as an intermediate structure during the transition from δ to γ -form by annealing.

Experimental

The syndiotactic polystyrene (sPS) was kindly supplied by Idemitsu Petro Chem. Co. Ltd. The weight-averaged molecular weight, M_w , was 2.1×10^5 , and the polydispersity index, M_w/M_n , was 2.8. The syndiotacticity was 99.8%. sPS pellet was dissolved into toluene (1 wt.%) at the temperature close to the boiling point. Subsequently the solution was cast on Petri dish at room temperature. Time-resolved small- (SAXS) and wide-angle (WAXS) X-ray scattering measurement (TR-SWAXS) was conducted at Photon Factory of High Energy Accelerator Research Organization (KEK), Japan. SAXS and WAXS were measured by one-dimensional position sensitive proportional counters. q -regions we could reach were $0.05 < q < 1.5$, $3.55 < q < 9.58$, $9.58 < q < 13.8$ (nm^{-1}) ($0.07^\circ < 2\theta < 2.11^\circ$, $5^\circ < 2\theta < 13.5^\circ$, $13.5^\circ < 2\theta < 26^\circ$), where 2θ is a scattering angle and q is the magnitude of scattering vector defined by $q = 4\pi/\lambda \sin \theta$. Here λ is the wavelength of the incident X-ray beam.

Results and Discussion

We observed the crystal modification of δ -form sPS specimen cast from toluene solution (1 wt.%) as a function of temperature. TR-SWAXS was measured with increasing temperature from 30 to 210°C at the rate of

2°C/min. WAXS data was measured by every ten degrees centigrade, where we can see δ - to γ -form transition around 120°C and γ - to α -form transition around 170°C. From 30 to about 140°C, two distinct peaks were observed around 7.8 and 10.2°, which are typical to δ -form of sPS. From 120 to about 190°C, a new distinct peak appeared at 9.2°, which is typical to γ -form of sPS. Finally from 170 to 210°C, new distinct peaks appeared at 6.7 and 11.5°, which are typical to α -form of sPS. Note that no significant peaks of δ_c -form (at 8, 14 and 21°) was observed during δ - to γ -form transition.

SAXS data was obtained simultaneously with WAXS described above by TR-SWAXS technique. One broad peak, which can be attributed to crystal-amorphous long period, was seen to move discontinuously around 120 and 190°C. The peak positions for δ -, γ - and α -form were specific to the respective structures, and they were reproducible.

Finally we investigated the structural change or mechanism for the transition from δ - to γ -form. We concentrated on the thermal changes of the normalized lattice spacings typical to δ -, γ - and α -form. From 30 to about 130°C, (010) and (210) lattices were observed. They seem to have similar temperature dependence in the temperature region except 55 – 80°C. This slope is close to that of (200) of γ -form observed at 140 – 190°C and those of (110) and (300) of α -form observed at 180 – 210°C. This slope is considered to be the thermal expansion coefficient of crystalline sPS, and is close to that of amorphous sPS ($\sim O(10^{-4})$). More interesting thing observed here is that (010) and (210) lattice spacings showed discontinuous change at the temperature region of 55 – 80°C. Especially (210) lattice spacing dramatically increased in this region. Solvent molecules are located between the sPS main chains along $\langle 210 \rangle$ direction. The fact that (210) lattice spacing increased means that solvent molecules gained enough room for the successive removal from the clathrate. Actually the solvent molecules removed from the crystal as the temperature reached the glass transition temperature of sPS ($\sim 120^\circ\text{C}$). Consequently the δ - to γ -form modification took place. This solvent evaporation was also observed by the thermal gravity analysis (though the data was not shown here).

References

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* okamoto.shigeru@nitech.ac.jp