Journal of Molecular Structure 1124 (2016) 98–102

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Investigation on the overlapping bands of syndiotactic polystyrene by using 2D-IR spectroscopy

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ARTICLE INFO

Article history:
Received 31 December 2015
Received in revised form
30 March 2016
Accepted 30 March 2016
Available online 1 April 2016

Keywords:
Syndiotactic polystyrene
Mesophase
Chain conformation
FTIR
Two-dimensional correlation spectroscopy

ABSTRACT

In this work, WAXD and FTIR spectroscopy were utilized to investigate the phase transition of syndiotactic polystyrene (sPS) from amorphous phase to mesophase during the isothermal annealing process at 130 °C. Two dimensional (2D) correlation infrared spectroscopy was applied to reveal the sub-bands from the highly overlapping bands. The ~900 cm^{-1} band is shown to be composed of two sub-bands. One band located around 906 cm^{-1} corresponds to the amorphous phase, another peak that occurs around 900 cm^{-1} is associated with mesophase. The trans-planar conformation band at 1223 cm^{-1} turns out to consist of two bands which might be related to trans-planar conformation with different sequence lengths.

1. Introduction

Syndiotactic polystyrene (sPS) attracts great attention because of its excellent properties including high melting temperature, low dielectric property and superior mechanical performance [1]. From the molecular structure point of view, sPS exhibits unusual polymorphic behavior. According to the literature, sPS may crystallize in five forms depending on experimental conditions [2,3]. Moreover, sPS may also form two mesophases [4–8]. In one mesophase, the polymer chains adopt trans-planar conformation [4,7,9], and in another mesophase, the sPS chains are in s(2/1)2 helical conformation [6,8]. Various experimental methods such as DSC, WAXD, SAXS and FTIR etc., have been applied to investigate the phase transitions of sPS [10–13] since deep understanding on the phase behavior is helpful to improve the final performance of sPS. Among these methods, FTIR spectroscopy has been extensively used as it provides abundant information concerning the conformation of the molecular chains of sPS in different phases [9,14–18]. To some extent, however, understanding on the spectral behavior of sPS in detail is limited by the band overlapping problems [19]. From this aspect, revealing sub-bands from complex congested envelop by using advanced spectroscopic methods will be helpful to enhance our understanding on the spectral behavior of sPS.

Two-dimension correlation spectroscopy proposed by Noda in the late 1980s [20–22], provides an alternative method to reveal the overlapping bands. The method is based on the analysis of a set of spectra that are sequentially acquired under some forms of perturbation applied to the sample. The spectra are transformed into a correlation intensity plot on a spectral plane defined by two independent spectral variable axes. Many spectral features that are not readily accessible in the original 1D spectra can be clearly visualized in the 2D spectra. Over the past thirty years, a large amount of research work on 2D correlation spectroscopy has been accumulated in the literature [23–28]. Among these researches, a lot of work dealt with polymeric systems and remarkable progresses have been achieved [29–33]. In many investigations, variable temperature has been adopted as the most popular external perturbation since it may induce many conformation changes, phase transitions and chemical changes [34–37]. However, the temperature-variable perturbation may also bring about changes on peak position and bandwidth of characteristic bands [38,39]. Such changes may induce cross peaks that have nothing to do with overlapping bands [40–42]. Consequently, this may lead to interference on the analysis of overlapping bands.

Herein we design a sample-specific experiment to construct 2D asynchronous spectra according to our investigation on the basic

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http://dx.doi.org/10.1016/j.molstruc.2016.03.103
0022-2860/

phase behavior of sPS. Firstly, sPS film in amorphous phase was prepared. Then the film was annealed at 130 °C for 2 h. Under this temperature, phase transition occurs from amorphous phase to mesophase in which the sPS chains are in trans-planar conformation. This process is long enough so that a series of FTIR spectra can be recorded and 2D correlation spectrum is generated to reflect the transition process. During the entire process, only amorphous phase and a mesophase are involved. Thus the obtained FTIR spectra are simplified since sPS in other phases do not exist in the sample film. Moreover, the phase transition is an isothermal process so that interference cross peaks caused by temperature variable process can be avoided. This forms a reliable basis for analysis of the overlapping bands of sPS.

2. Experimental

Syndiotactic polystyrene (sPS) ($M_w = 2.1 \times 10^5$, $M_w/M_n = 2.2$, syndiotacticity (rr) = 99%) was kindly provided by Dow Chemicals. The sPS film was prepared by melt-compression at 290 °C for 10 min, followed by quenching into an ice-water mixture quickly. The obtained quenched sPS film was about 20 μm in thickness.

In-situ wide angle X-ray diffraction (WAXD) experiment was carried out at the beamline 1W2A-SAXS [43] in the Beijing Synchrotron Radiation Facility (BSRF). In the experiment, a Linkam (LTS350) hot stage was utilized. The distance between the sample film and detector was 144 mm and the wavelength of the X-ray was 1.54 Å. The resolution of MAR-CCD (MAR-USA) detector was 2048 × 2048 pixels with each pixel size of 79 μm × 79 μm. The quenched sPS film was heated to 130 °C at 60 °C/min and maintained for 2 h to obtain the WAXD patterns.

In-situ Fourier transform infrared (FTIR) spectroscopy measurements were carried out on a Nicolet 6700 (Thermo Fisher Scientific) FTIR spectrometer equipped with a Linkam FTIR 600 hot stage. The quenched sPS film was sandwiched between two thin KBr plates. For the isothermal process, the sample was heated to 130 °C at 60 °C/min and then retained at that temperature for 2 h. The spectra were obtained by co-adding 16 scans at a resolution of 4.0 cm^{-1}. The spectra were collected at a constant time interval of 1 min during the annealing process. The obtained IR spectra were subjected to a linear baseline correction to minimize the effect of baseline. The 2D-IR correlation spectra were generated by using the '2D Shige' software written by Shigeaki Morita (Kwansei Gakuin University, Sanda, Hyogo, Japan).

3. Results and discussion

Before analyzing the infrared spectra of sPS, the initial state of sPS in amorphous phase and phase transition process from amorphous phase to mesophase at 130 °C were characterized by using in-situ WAXD experiments. The WAXD intensity profile of the initial sPS film is shown in Fig. 1 (the bottom trace). The observation of two characteristic broad halos at 10.6° and 19.4° confirms that only amorphous phase exists in the initial sPS film obtained by quenching the molten sPS into ice-water mixture. Additionally, the WAXD intensity profiles of the sPS film annealed at 130 °C for different time are also illustrated in Fig. 1. A board peak at 12° and a relatively sharp peak at 20.4°, which are the characteristic diffraction peaks of sPS mesophase, appear upon the annealing process. During the entire annealing process, characteristic peaks for sPS in other forms are not observable, only the amorphous phase and the mesophase are involved. Thus the system is simplified. The WAXD intensity profiles were analyzed by using the 'PeakFit' software and the content of amorphous phase and mesophase are characterized by X_{am} and X_{meso} defined in Eq. (1) and Eq. (2) listed below:

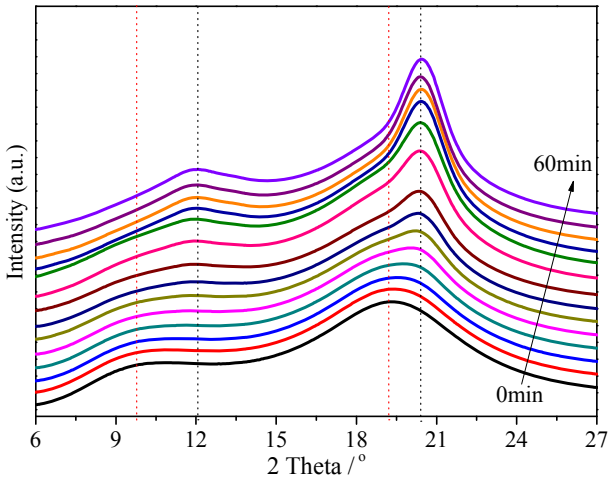

Fig. 1. Selected 1-D WAXD curves of the sPS amorphous film annealed at 130 °C for different time.

$$X_{am} = \frac{Area_{am}}{Area_{am} + Area_{meso}}. \quad (1)$$

$$X_{meso} = \frac{Area_{meso}}{Area_{am} + Area_{meso}}. \quad (2)$$

Fig. 2 depicts the variation of X_{am} and X_{meso} as a function of annealing time. The content of mesophase increases while amorphous phase decreases at the initial stage of the annealing process. When the annealing time exceeded 50 min, the contents of mesophase and amorphous phase approach asymptotically constant values.

The above isothermal phase transition system provides us an ideal chance to study the FTIR spectral behavior of sPS by using 2D correlation spectroscopy based on the following reasons:

1. Only two phases are involved, interference of characteristic bands of sPS in other phases is not present.
2. Phase transition brings about remarkable spectral changes, this makes it possible to obtain 2D correlation spectrum with high signal-to-noise level.

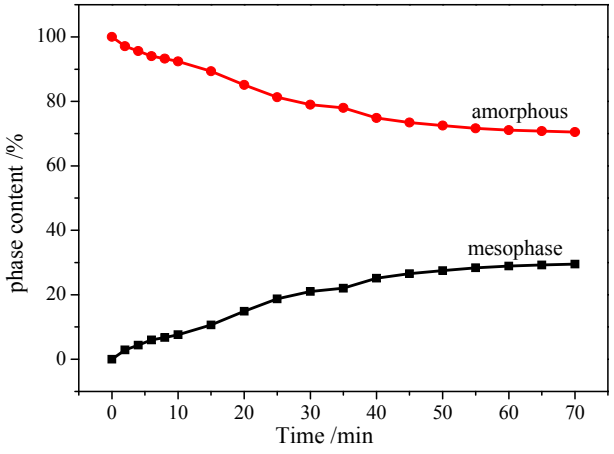

Fig. 2. The fractions of mesophase and amorphous phase of sPS during isothermal annealing.