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A technique to measure the crystallinity of syndiotactic polystyrene using thermal analyses

D. H. Krzystowczyk*, X. Niu, R. D. Wesson, and J. R. Collier

Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803, USA

Summary

A simple method for using differential scanning calorimeters to determine the crystallinity of syndiotactic polystyrene has been developed. Its validity was confirmed by use of infrared and x-ray analysis, as well as comparison to data from the literature. This method will be used to determine the effect of nucleating agents, shear stress, and temperature on the crystallization kinetics of syndiotactic polystyrene.

Introduction

In recent years, syndiotactic polystyrene (sPS) has enjoyed intense industrial and academic interest due to several desirable physical properties (high melt temperature, high crystallinity, rapid crystallization rates). Several crystallographic forms of sPS are attainable, and are generally refered to as α, β, δ, and γ. The α form consists of hexagonal unit cells, and contains zig-zag, or trans-planar backbones. The β form also contains the zig-zag backbone, but this conformation contains orthorhombic unit cells. By contrast, the δ and γ forms contain helical backbones and arise due to solvent induced crystallization (1). In addition, recent work has shown that a third phase, a mesophase, can exist in sPS. de Candia et al. (2) were the first to report this, and further evidence was provided by others (3-5).

A conformationally sensitive IR band has been reported in sPS at 1222 cm^{-1}. Absorbance at this band is due to "CCH bending of the CH_2 and CH groups and CC backbone stretching" (6) present in planar trans-trans bonds. This band has therefore been widely used to indicate the formation of crystals from the melt by several researchers (7-11). This band is completely absent in amorphous sPS (6,12).

Filho and Vittoria (7) used absorbance at this band as a measure of crystallinity. They corrected for different film thicknesses by normalizing the intensity at the 1222 cm^{-1} peak by dividing the intensity of a reference peak at 1183 cm^{-1}. To relate the IR absorbance ratio to crystallinity of their samples, they used a technique that employed sorption of dichloromethane. DSC methods to determine crystallinity were not used because "during the heating in the DSC further crystallization occurs, making impossible the determination of the degree of crystallinity with the DSC technique." (7) Others reached the same conclusion (1,13,14).

The problem may lay in the complex conformational and phase transitions exhibited by sPS. At temperatures between the glass transition and melting point, sPS is known to equilibrate between its crystallographic forms. In addition, there is the further complication of the mesophase. The mechanics of these transitions are not completely known. It is possible to expect that any or all these transitions may be accompanied with heat effects that act to mask the DSC trace.

An improvement of the DSC method was developed by our group. This involves rapid heating of sPS samples so as to limit the time allowed for the transitions.

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*Corresponding author

Experimental

sPS, provided by Dow Chemical ($\bar{M}_w = 458{,}000$, $\bar{M}_w / \bar{M}_n \sim 2.5$), was made into rectangular films approximately 0.25 mm thick by use of a computer controlled experimental hot press. Film samples were analyzed on a Perkin-Elmer FT-IR Spectrometer 1760X. The samples were shot at a resolution of 0.5 cm^{-1}, over the range of 1800 - 600 cm^{-1}. Each sample was analyzed twice, with 30 scans performed each analysis. For this work, the raw intensities of the absorbances at 1222 and 1183 cm^{-1} were used, and not the integrated areas or calculated peak heights. The reason for this method will be discussed later.

The same samples were then analyzed on a Seiko Instruments DSC220C, with a typical run including temperature profiles ranging from -100 - 350 °C. A heating rate of 80 °C/minute was used. Two analyses were performed for each sample to ensure uniformity.

Results and Discussion

DSC scans revealed crystallization and melting peaks. The crystallization peak generally displayed a maximum at 150 °C, and represented melt crystallization of the initial amorphous content of the sample. The melting peak begins around 250 °C, peaking at about 270 °C. This represents the melting of all crystals present.

The fractional crystallinity of the samples was determined by ratioing the areas under the two peaks. This method is described below:

$$X_c = (\Delta H_m - \Delta H_c)/\Delta H_m^{\circ}$$

where ΔH_m is the heat absorbed during melting, ΔH_c is the heat release upon crystallizing, and ΔH_m° is the theoretical heat absorbed during melting for fully crystalline samples. A value of 53 mJ/mg was obtained by extrapolating the crystallinity - melting enthalpy data of de Candia, Filho, and Vittoria (2).

Sample	Crystallinity	Peak Ratio
H-25	0	0.313
H-17	0.06	0.347
H-18	0.09	0.370
H-9	0.10	0.480
H-15	0.23	0.612
H-39	0.40	0.877
H-16	0.41	0.811
H-29	0.41	0.855
H-49	0.41	0.899
H-38	0.42	0.901
H-42	0.43	0.887
H-30	0.45	0.870
H-31	0.45	0.866
H-41	0.46	0.890
H-14	0.46	0.917
H-36	0.47	0.902
H-2	0.48	0.996

Table 1 Experimental DSC and IR data.

In order to confirm this method, a film sample was prepared at conditions known to lead to the amorphous phase (sample H-25, held at 320°C for 3 minutes, then quenched in ice water). The rapid heating DSC method yielded a lack of any appreciable crystallinity in the sample (ie the melt enthalpy equaled the crystallization enthalpy). This lack of crystallinity was confirmed by x-ray analysis. DSC runs at lower scan rates (10°C/min - 40°C/min) did not yield the low crystallinity known to exist, but instead gave levels around 10%.

Raw intensities of the absorbance at 1222 and 1183 cm^{-1} were ratioed. As with the work done by Filho and Vittoria, the 1183 cm^{-1} peak was used as a reference peak to correct differences in sample thicknesses. Averaged results from 17 samples are shown in

Table 1. Figure 1 is a plot of the IR absorbance ratio of each sample plotted against the fractional crystallinity as determined by our DSC method.

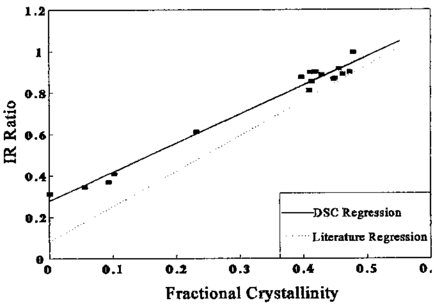

Fig. 1 Experimental and literature values of IR intensity ratios of annealed sPS samples.

A straight line is obtained from a regression of our data with an r^2 of 0.98, as shown by the solid line on Figure 1. By comparison, the regression from the six points used of the Filho and Vittoria (7) data was 0.99, and is represented by the dotted line on Figure 1. The crystallinity relationship developed by their work was confirmed by Wang et al. by use of changes in the heat capacity at the glass transition point (14).

A lack of data were obtained at intermediate crystallinities. This is probably due to the very rapid crystallization rates of sPS. Filho and Vittoria pointed out that a two-step mechanism is involved in the crystallization process, and the data we collected probably confirms this. All samples with a crystallinity of less than 0.40 can probably be assumed to be crystallized during the more rapid first step. It may be that the point of separation is related to the formation of the mesophase, and that low levels of crystallinity are actually short range order and therefore mesophase.

The IR data used were simple raw absorbance numbers, and therefore the peak ratio did not go to zero at zero crystallinity. This raw data was used to show that simple, inexpensive IR equipment can be used effectively for this method. This relationship is being used to perform crystallization studies on nucleated and sheared sPS samples.

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