An Interpretation of the Formation of α- and β-Form Crystals in Bulk Syndiotactic Polystyrene

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ABSTRACT: The crystallization of the α- and β-form crystals of syndiotactic polystyrene (sPS) is determined by the crystallization temperature. Being crystallized at various temperatures from the melt, sPS forms the β form crystal at high temperatures above about 230 °C, α form crystal at low temperatures below about 170 °C and a mixture of the α and β form at intermediate temperatures.

Introduction

Syndiotactic polystyrene (sPS) has received considerable attention as one of a number of potential engineering plastics, due to its high melting temperature, fast crystallization rate, and good chemical resistance.[1] Of particular interest is its complex polymorphic behavior involving four crystalline forms: α, β, γ, and δ. It has been shown that the α and β forms, both containing planar zigzag chains with an identity period of $c = 5.1$ Å, can be obtained from the melt or the glassy state of sPS under different thermal conditions,[2−4] while the forms γ and δ, both containing (2/1)2 helical chains with an identity period of $c = 7.8$ Å, are formed under conditions where solvents are involved.[5,6] Among these four crystalline forms, the α form with a hexagonal unit cell with $a = 26.26$ Å and the β form with an orthorhombic unit cell with $a = 8.81$ Å and $b = 28.82$ Å [7] are more concerned with practical applications, since their formation is directly related to the processing and final mechanical properties of sPS products.

There are only a few papers reporting the formation of α- and β-form crystals from sPS.[2−4,7] Guerra and coworkers[2] first gave the nomenclature of these two crystalline forms and studied their formation from the melt and the glass phase of sPS in detail. Their results showed that the cooling rate from the melt and the thermal history of the melt are the major factors influencing the formation of these forms. When sPS was cooled at a moderate cooling rate from the melt, its β form can be obtained if no α-form memory remains in the melt; otherwise, the α form will be produced. The α form can also be obtained by quenching from the melt or by annealing from the amorphous phase. However, no further work appears and a deep understanding of the formation of both crystalline forms is still lacking.

In this paper, the effect of crystallization temperature on the formation of the α- and β-form crystals of syndiotactic polystyrene (sPS), without any thermal history in their melt, has been investigated systematically. The interpretation of the results combined with results reported in the literature has been attempted.

Experimental Section

The sPS was synthesized in Prof. Hu Youliang's group.[8] The polymer has a M_w of 96 000 and a M_w/M_n of 4.6, as determined by GPC and a syndiotacticity of 97%, as determined by high resolution NMR. Its T_m is 267 °C.

The determination of the sPS crystalline forms was conducted by infrared spectroscopy with a Perkin Elmer 2000 FTIR spectrometer at a resolution of 2 cm^{-1}. The wavenumber range scanned was 1300−850 cm^{-1}, with 10 scans collected. It has been shown [9] that the α-form crystal exhibits a characteristic band at 902 cm^{-1}, while the β form appears at 911 cm^{-1}. Because of the overlapping of these two bands of coexisting forms in one sample, the quantitative evaluation of the content of each form is difficult. So the measurement of the content of the α and β forms was carried out with the help of wide-angle X-ray diffraction analysis, according to the method described in ref 2.

Wide-angle X-ray diffraction (WAXD) patterns were obtained with nickel-filtered Cu Kα radiation. From the patterns of the diffractometer, quantitative evaluations of the content of the two crystalline forms possibly present in the melt-crystallized samples were also obtained. The 2θ region 10−15° was considered, and a baseline between the two intensity minimal located at 2θ =10.8° and 2θ =14.8° is drawn. The areas (A) of the two peaks located at 2θ =11.6° and 2θ =12.2° were measured, and the content percentage of the α form in the crystalline fraction was evaluated by the approximate relation

$$P_\alpha = \frac{1.8A(11.6)/A(12.2)}{1 + 1.8A(11.6)/A(12.2)} \times 100$$

where 1.8 was the ratio between the intensities (measured under the same experimental conditions) of the peaks at 11.6 and 12.2° for samples of equal thickness and crystallinity in the pure α and β forms, respectively.

The films for the infrared and wide-angle X-ray diffraction measurement were all made having a thickness about 0.05 mm in the following way. For the crystallization from the melt, the sPS powder was sandwiched between two cover glasses of 0.16 mm thick and heated on a hot stage at 320°C. The sPS was pressed into the film first and kept for 5 min. This process proved to be enough to eliminate any thermal history and the memory of the α-form in the melt. The sample was transferred quickly (in 1−2 s) from the hot stage to a silicon oil bath kept at seven desired crystallization temperatures (T_c), and crystallized there. The crystallization time at each T_c was 20 min, except for 60 min at 250 °C, due to a slow crystallization rate at this temperature.

Results and Discussion

The FTIR spectra of sPS crystallized at different temperatures, T_c's, after quenching from melt to T_c, are shown in Figure 1. It is seen that for samples crystal-

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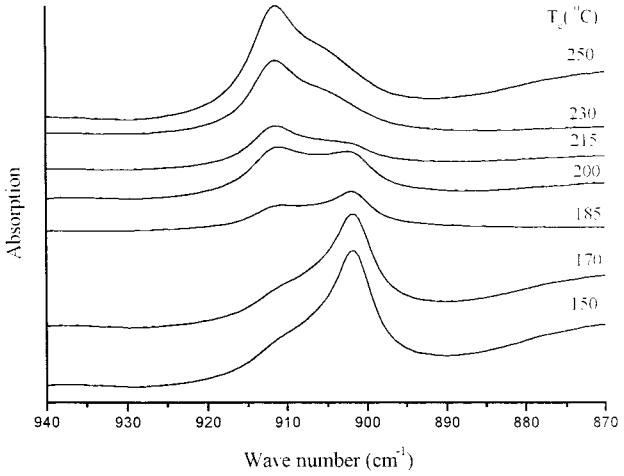

Figure 1. FTIR spectra of sPS films crystallized at different temperatures, T_c's, after quenching from melt to T_c.

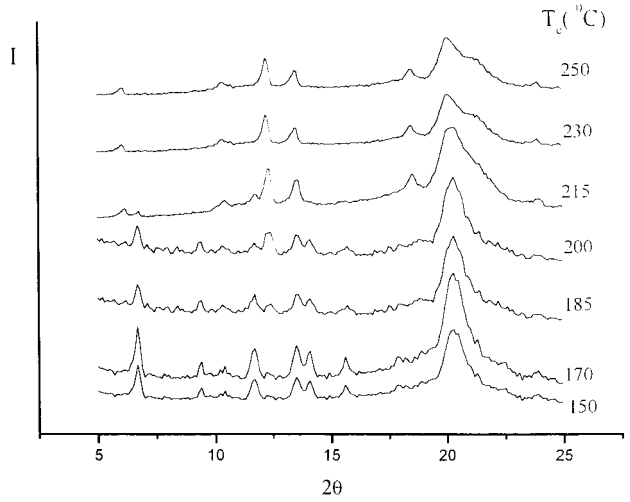

Figure 2. X-ray diffraction patterns (Cu Kα) of sPS films crystallized at different temperatures, T_c's, after quenching from melt to T_c.

lized at 250 and 230 °C, only a band at 911 cm^{-1} appears, together with a shoulder close to 906 cm^{-1} due to the presence of the amorphous. This indicates that sPS in the β form has been obtained. As T_c further decreases, the α-form crystal begins to form as well, shown by the appearance of an absorption at 902 cm^{-1}. At 200 °C, almost the same absorbance at 902 and 911 cm^{-1} indicates nearly the same amount of the α- and β-form crystals produced at this temperature. When crystallized at 185 °C, the film has a content of the α form exceeding that of the β form; and at 170 or 150 °C, the film was in the pure α form, shown by the appearance of a lone band at 902 cm^{-1}.

The X-ray diffraction patterns of the sPS samples, showing the same results as the FTIR spectra, are reported in Figure 2. For a crystallization temperature above 230 °C, there are only the typical β form peaks present at $2\theta = 6.1$, 12.2, and 18.6° and so on. For a low crystallization temperature up to 170 °C, only α forms are present (e.g., the peaks at $2\theta = 6.7$, 11.6°). When crystallized between 170 and 230 °C, mixed (α + β)-form crystals can be obtained, and the amount of the α form in the samples increases with decreasing crystallization temperature. The percentages of the α form in the crystalline phase, evaluated for the samples crystallized at 185, 200, and 215 °C, are about 80%, 50%, and 15%, respectively.

These results clearly indicate that the crystallization temperature (or the degree of supercooling) is the intrinsic factor controlling the formation of the α- and β-form crystals. The pure β form is only produced at high temperatures above about 230 °C. The pure α form is present at low temperatures below about 170 °C. In the intermediate temperature range between 170 and 230 °C, both forms of the crystal coexist.

When the sPS crystallizes from melt, pure α- and β-form crystals, or mixed (α + β)-form crystals can be obtained, depending on the crystallization condition. In a previous paper it has been shown that β-form samples were obtained at low cooling rates while α-form samples could be obtained under quenching conditions. The effects of different cooling conditions were considered in more detail. However, the temperature dependence of the α- and β-form crystals of sPS shown here has not been reported in the literature up to now. A thermodynamic consideration may be needed to get insight into this case.

Since the β form crystallizes at a high temperature from the melt, it will crystallize first during cooling. At low cooling rates, the crystalline phase of the β form has almost reached the maximum crystallinity of the sample by cooling to 230 °C. So even as the temperature for the α-form formation is reached, there is no more crystallizable sPS portion remaining for the α-form formation. The observed β form in the sample cooled to room temperature is that already formed before the sample is cooled to 230 °C. That is the reason the β form is always obtained by cooling at a slow or moderate rate. When the cooling rate is increased to such a value that the β form has no time to crystallize to the maximum crystallinity of sPS at high temperatures, then the α form has a chance to crystallize at low temperatures and both forms of crystals coexist. This can be proved by the observation of De Rosa et al.,[7] where the amount of the α form increases with increasing cooling rate. If cooling rate is high enough that the β form has almost no time to crystallize at high temperature, only the α form can crystallize at low temperature. That is the reason only the α-form crystal is obtained under quenching conditions.

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