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Effects of crystallization temperature on the polymorphic behavior of syndiotactic polystyrene

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Abstract

The influence of crystallization temperature on formation of the α- and β-form crystals of syndiotactic polystyrene (sPS) was investigated by X-ray diffraction and non-isothermal differential scanning calorimetry analysis. For sPS samples without any thermal history, the crystallization temperature must be the intrinsic factor controlling the formation the α and β-form crystals. Being crystallized at different cooling rate from the melt, sPS forms the β-form crystal until the temperature cooled down to about 230 °C, and α-form crystal can only be obtained when the temperature was below about 230 °C. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Syndiotactic polystyrene; Polymorphism; Crystallization temperature

1. Introduction

Syndiotactic polystyrene (sPS) has received considerable attention as a potential engineering plastic due to its high melting temperature, fast crystallization rate and good chemical resistance [1]. Since Ishihara et al. first obtained sPS [2], more and more studies [3–6] have been carried out on sPS, scrutinizing the synthesis and copolymerization. Now the catalysts for syndiotactic polymerization of styrene are distinguished into two categories, i.e. titanocene and non-titanocene [7,8].

The existence of polymorphic sPS structures depending on the crystallization condition from melt or solution is also of particular interest. In fact, some papers [9–15] have been published on the four types of crystalline forms (α, β, γ and δ) and two mesomorphic forms of this new material. It has been shown that both the α- and β-forms have an all-*trans* planar zigzag $(tttt)_n$ backbone conformation, whereas the γ- and δ-forms have a helical (*trans*, *trans*, *gauche*, *gauche*, $(ttg^+g^+)_n$) backbone conformation. The α-form with a hexagonal unit cell and the β-form with an orthorhombic unit cell, both with an identity of $c = 5.1$ Å, can be obtained from the melt or the glassy state of sPS under different thermal conditions [9,10]. The γ- and δ-forms, both with an identity of $c = 7.8$ Å, can only be formed from solvent swelling of glassy sPS and have been shown to have the same monoclinic crystal structure. Among these four crystalline forms, the α-form with $a = 26.26$ Å and the β-form with $a = 8.81$ Å, $b = 28.82$ Å are the primary crystalline polymorphs and result from different thermal and pressure treatments above the glass transition temperature (T_g). Because there is almost no energy difference between the two known polymorphs having the all-*trans* conformation [16], the transformation of the α-form to the β-form is hardly implemented even at temperatures close to the melt point [17]. Further, each of them can be divided into two types based on different degrees of structural orders [11,12]. The two limited disordered modifications are known as α′ and β′, respectively, and two limited ordered modifications are referred to as α″ and β″. This means that *α-form* is a general designation of α′ and α″, and *β-form* of β′ and β″. In general, being crystallized from the melt, sPS forms the β′-form crystal or α″-form crystal because of different crystallization conditions [13].

A number of studies [9–18] have been carried out on polymorphs of sPS. X-ray diffraction, electron diffraction, Fourier-transformed infrared (FTIR) spectroscopy and solid-state nuclear magnetic resonance (NMR) have been used in the recognition and quantification of the different

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polymorphs in polymeric materials. Guerra and his co-workers [9,12] first gave the nomenclature of the α- and β-crystalline forms and studied their formation from melt and 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. The formation of the α-form is a kinetically controlled process, meanwhile the β-form crystal structure is more stable thermodynamically. If the memory effect of nuclei is eliminated by heating to higher temperature and cooling sPS down at a moderate cooling rate (say less than 20 °C/min) from the melt will lead to the formation of its β-form, otherwise the formation of α-form. The α-form can also be obtained by quenching from the melt or by annealing from the amorphous phase. The intensities and the Bragg distance observed in the powder patterns for the α- and β-modifications have been given by Guerra et al. [9]. Ho et al. [13] also discussed the effects of maximum annealing temperature, the cooling rate to the crystallization temperature, crystallization temperature and crystallization time on the polymorphism of melt-crystallized sPS, using the metastability theory given by Keller and Cheng [19]. Even the polymorphic crystal forms of sPS in miscible states and in thin film have been investigated by Woo et al. [20] and Wu et al. [21].

At the same time, there is a considerable interest in understanding the crystallization of sPS. Cimminno et al. [22] and Lawrence et al. [23] have described the kinetics of isothermal crystallization of sPS using differential scanning calorimetry (DSC). The crystallization kinetics of sPS under non-isothermal conditions has also been analyzed by Wesson [24]. Though the formation of the α- and β-forms is closely related to the crystallization kinetics of each kind of crystal (especially non-isothermal crystallization kinetics), to date, there is no paper that involves both polymorphism and non-isothermal crystallization kinetics at the same time to study the polymorphic behavior of sPS.

Our previous study [18] scrutinized the effect of crystallization temperature on the formation of the α- and β-form crystals of sPS without any thermal history by using infrared spectroscopy and X-ray diffraction. The 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 approximately above 230 °C. The pure α-form is obtained at low temperatures approximately below 170 °C. The intermediate crystallization temperature range between 170 and 230 °C results in coexistence of both crystal forms.

In this paper, X-ray diffraction and non-isothermal DSC analysis have been combined to answer the question: which is the more significant factor controlling the formation of the α and β-form crystals for sPS samples without any thermal history—the crystallization temperature or the cooling rate from the melt?

2. Experimental section

2.1. Materials

The sPS was synthesized in Prof. Hu Youliang's laboratory. A novel non-titanocene (titanium β-diketonate complexes/MAO and titanium 8-hydroxyquinolinate complexes/ MAO) catalyst was used to synthesize sPS, according to the method described in Ref. [8]. The polymer has its M_w of 630000 and M_w/M_n of 4.5, as determined by GPC and a syndiotacticity of 97%, as determined by high resolution NMR. Its T_m is 272 °C.

2.2. Wide-angle X-ray diffraction (WAXD)

The X-ray diffraction experiments were performed using a Rigaku RINT 2200 diffractometer system consisting of a rotating anode generator and wide angle powder goniometer fitted with a high-temperature attachment. The generator was operated at 40 kV and 30 mA. The sample holder was an aluminium block, and a thin film of the sample was formed on that block by melt pressing the sample. The effects of the background have been eliminated by computer program. Each sample was used only once in order to avoid the influence of other factors, e.g. thermal degradation. The samples were initially heated in a hot stage at 340 °C and kept for 5 min. This process was sufficient to eliminate any thermal history and the memory of the α-form in the melt [18,22,23]. Then some samples were cooled at different cooling rates (2, 5, 10, 20, 40 and 80 °C/min) to certain temperatures (230 and 120 °C, respectively), and wide-angle X-ray diffraction (WAXD) was used to determinate the crystalline forms at 230 and 120 °C, respectively. The scanning 2θ angle ranged between 5 and 40° with a scanning rate of 5°/min. Other samples were quenched to 230 °C at a rate of 120 °C/min by a programmed procedure (during this course, there was no crystallization at all, see Fig. 5), and then cooled at different cooling rates (2, 5, 10, 20, 40 and 80 °C/min) to 120 °C. Wide-angle X-ray diffraction (WAXD) scanning was carried at 120 °C. The preparation of X-ray diffraction samples is shown schematically in Fig. 1.

The determination of the sPS crystalline forms was conducted by WAXD, and diffraction patterns were

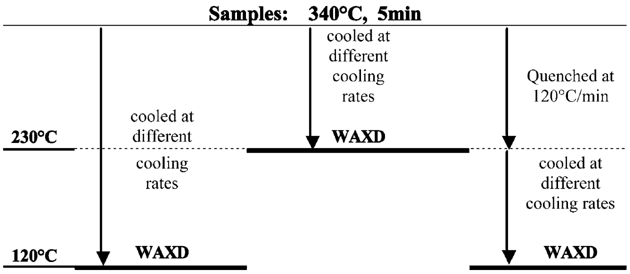

Fig. 1. Schematic representation of the preparation of X-ray diffraction samples.

obtained with nickel-filtered Cu Kα radiation. It was seen that the α-form crystal exhibits characteristic peaks at $2\theta = 6.7$, 11.6°, while the β-form at $2\theta = 6.1$, 12.2 and 18.6°. The measurement of the content of the α and β-forms was carried out according to the method described in Ref. [9]. The 2θ region, 10–15°, was considered, and a base line between the two intensity minimal located at $2\theta = 10.8°$ and $2\theta = 14.8°$ was drawn. The areas (A) of the two peaks located at $2\theta = 11.6°$ and $2\theta = 12.2°$ were measured, and the percentage of the α-form in the crystalline fraction was evaluated by the approximate relation [9]

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

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 the samples of equal thickness and crystallinity in the pure α- and β-forms, respectively.

2.3. Non-isothermal DSC analysis

The non-isothermal crystallization behaviors of sPS samples were investigated by using a Perkin–Elmer DSC-7 differential scanning calorimeter. Before the data gathering, all the samples were heated to 340 °C and held in the molten state for 5 min to eliminate the influence of thermal history. All operations were carried out under a nitrogen environment. The samples' weights were between 4 and 7 mg.

Non-isothermal crystallization experiments were carried out by cooling samples from 340 °C to an ambient temperature using different cooling rates. The exotherm as a function of temperature was recorded with the cooling rates of 2, 5, 10, 20, 40 and 80 °C/min, respectively.

Nakamura et al. [25] suggest the relative crystallinity, $X(t)$, in semicrystalline polymers may be expressed as

$$X(t) = 1 - \exp\left\{-\left[\int_0^t K(T)\,\mathrm{d}t\right]^n\right\}$$

where $K(T) = k(T)^{1/n}$, and n is related to the crystal growth dimension. This equation assumes as a first approximation that the system is isokinetic, i.e. the crystal growth rate divided by the probability to form new nuclei is constant and is not a function of temperature. The equation may be expressed as a function of temperature by incorporating the cooling rate transformation $\Phi = \mathrm{d}T/\mathrm{d}t$, giving rise to

$$X(T) = 1 - \exp\left\{-\left[\frac{1}{\Phi}\int_{T(0)}^{T(t)} [k(T)]^{1/n}\mathrm{d}T\right]^n\right\}$$

3. Result and discussion

3.1. Crystallization at different cooling rates

The X-ray diffraction patterns of the sPS samples, melted at 340 °C and then cooled at different cooling rates (2, 5, 10, 20, 40 and 80 °C/min) to 120 °C, are shown in Fig. 2. For low cooling rates up to 10 °C/min, the β-form (characteristic peaks at $2\theta = 6.1$, 12.2, 18.6°) is always present. For cooling rate higher than 80 °C/min, only typical α-form peaks (at $2\theta = 6.7$, 11.6°) are obtained. For cooling rates between 10 and 80 °C/min, both α and β-form crystals coexist, and the amount of the α-form in the samples increases with the cooling rate. The percentages of the α-form in the crystalline phase, calculated from WAXD patterns for the samples cooled at 10, 20, 40 and 80 °C/min, are about 0, 20, 75 and 100%, respectively. All these results are the same as the observation of Guerra et al. [9,12].

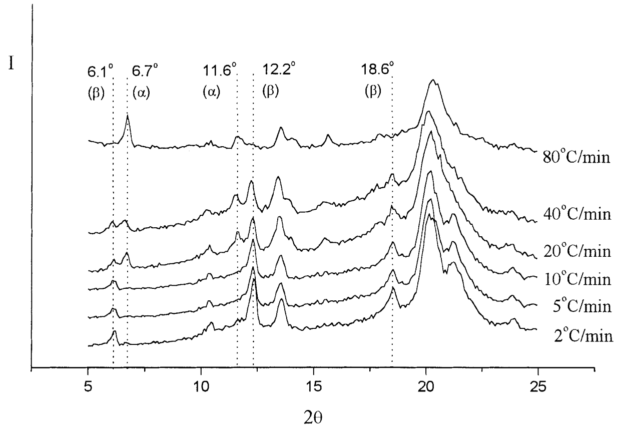

Fig. 2. X-ray diffraction patterns (Cu Kα) of sPS samples melted at 340 °C and then cooled at different cooling rates to 120 °C.

3.2. Crystallization at different temperatures

The X-ray diffraction patterns of the sPS samples, recorded at 230 °C (Fig. 3) are obtained from the samples cooled from 340 °C at different cooling rates

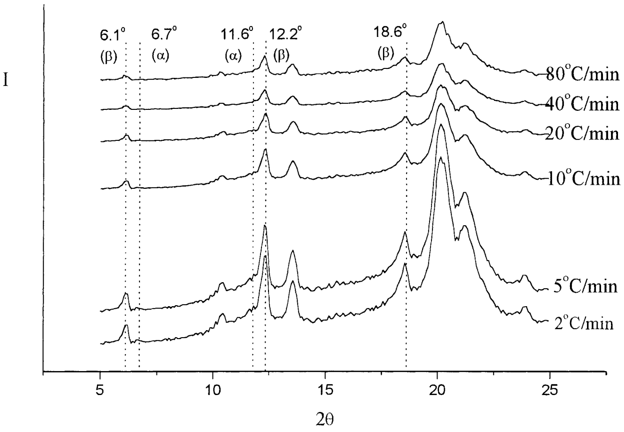

Fig. 3. X-ray diffraction patterns (Cu Kα), recorded at 230 °C, of sPS samples melted at 340 °C and then cooled at different cooling rates to 230 °C.

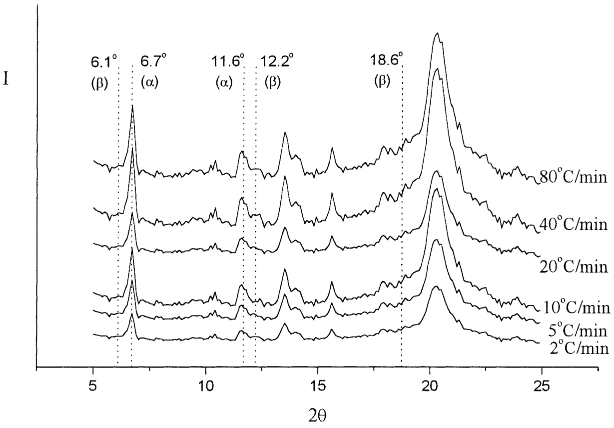

Fig. 4. X-ray diffraction patterns (Cu Kα) of sPS samples quenched from 340 to 230 °C and then cooled at different cooling rates to 120 °C.

(2, 5, 10, 20, 40 and 80 °C/min) to 230 °C. It is seen that for all the samples (cooled down to 230 °C at different cooling rates), only β-form peaks (at $2\theta = 6.1$, 12.2, 18.6°) appear, though some of the β-form crystals may be obtained just during the X-ray diffraction experiments at 230 °C. These do not conflict with our earlier results that pure β-form is only produced at high temperatures above about 230 °C. Above about 230 °C, even though the cooling rate from the melt is high up to 80 °C/min, the α-form crystals are not formed. This result clearly indicates that the cooling rate from the melt should not be the major factor influencing the formation of α- and β-forms at least when the crystallization temperature is higher than 230 °C.

Fig. 4 shows the X-ray diffraction patterns of the samples quenched from the melt to 230 °C and then immediately cooled at different cooling rates (2, 5, 10, 20, 40 and 80 °C/min) to 120 °C. It can be observed that for all the samples (cooled down from 230 to 120 °C at different cooling rates), only α-form crystal characteristic peaks (at $2\theta =$ 6.7, 11.6°) exist. During this course, there are no β-form crystal peaks obtained, viz. no matter how slow the cooling rate is, only α-form can be obtained when crystallization temperature is lower than 230 °C. This is similar to the results shown in Fig. 3, i.e. the cooling rate from the melt should not be the major factor influencing the formation of α- and β-forms when the crystallization temperature is lower than 230 °C.

Both Figs. 3 and 4 definitely show the similar results, i.e. for both crystallization temperature range, above 230 °C or below 230 °C, the cooling rate from the melt is not the intrinsic factor controlling the formation of the α- and β-form crystals. And the crystallization temperature certainly seems to be an important influence. The α-form can only be obtained when the crystallization temperature is lower than about 230 °C, whereas the β-form can be obtained when the crystallization temperature is higher than about 230 °C.

3.3. Non-isothermal crystallization

The above conclusion looks as if it was quite different from the observation of Fig. 2 and Guerra et al. [9]. In fact, non-isothermal DSC analysis could supply a deep explanation of this difference in appearance. From a technological point of view, non-isothermal crystallization conditions are almost the same as those of X-ray diffraction experiments conducted in this study, so that the study of crystallization of sPS under non-isothermal conditions is of great importance. Because the non-isothermal crystallization is a temperature-changing process, the relative crystallinity increases with the temperature decreasing (or crystallization time prolonging). The plots of relative crystallinity with temperature are shown in Fig. 5. Relative crystallinity as a function of temperature was determined by fractionating the exothermic crystallization peak. Running integrals, which relate the total peak area to the area at a specified temperature, was used.

Fig. 5 shows that with the increasing of cooling rate, the onset crystallization temperature decreases evidently and the relative crystallinity of sPS at higher temperature drops rapidly. From Wesson's observation [24], similar conclusion has been obtained. For cooling rates lower than 10 °C/min, the relative crystallinities have reached almost the maximum of the sample by cooling to 230 °C. For cooling rates higher than 80 °C/min, there is almost no crystallization when the temperature cooled down to 230 °C. For cooling rates at 20 and 40 °C/min, the relative crystallinity of each sample is 80 and 25% approximately when the temperature cooled down to 230 °C. As we know, pure β-form is only produced at high temperatures above about 230 °C [18]. These relative crystallinities are just in accordance with the percentages of the β-form crystals estimated by X-ray diffraction. It can supply another evidence to prove the conclusions that for sPS, α-form can only be obtained when the crystallization temperature is lower than about 230 °C, whereas the β-form can only be obtained

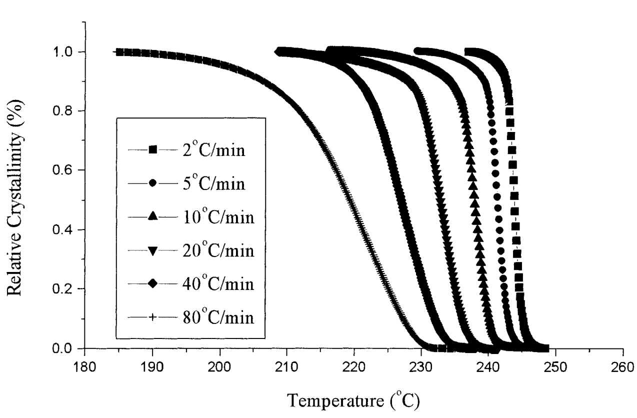

Fig. 5. Plots of relative crystallinity *versus* temperature for sPS samples cooled from 340 °C at different cooling rates to 120 °C, determined by DSC.

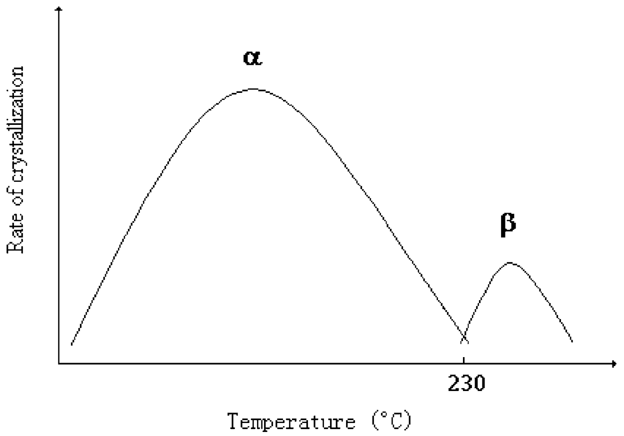

Fig. 6. Schematic representation of the crystallization rate of α and β-form crystals of sPS sample.

when the crystallization temperature is higher than about 230 °C. As shown schematically in Fig. 6, by comparing the crystallization rates of α- and β-form crystals, the maximum crystallization rate of α-form crystal is much faster than that of β-form crystal. But when the temperature is higher than about 230 °C, the crystallization rate of α-form crystal is too slow to be examined.

By combining with the results of Fig. 5, the difference among Figs. 2–4 can be explained as follows.

For sPS samples without any thermal history, since the β-form crystallizes at high temperature from the melt, it will first crystallize during cooling until the temperature cooled down to about 230 °C, and then the α-form will have a chance to crystallize. At low cooling rates up to 10 °C/min, the relative crystallinities have almost reached the maximum of the sample before cooling to 230 °C (Fig. 5). During this course, only β-form crystals can be formed. So even the temperature for the α-form formation is reached (below 230 °C), there is no more crystallizable sPS portion for the α-form formation. The observed β-form in the sample cooled to room temperature is that already formed before the sample being cooled to 230 °C. This is the reason why only β-form can be obtained when sPS is cooled down at a slow or moderate cooling rate from the melt. For cooling rate higher than 80 °C/min, there is almost no crystallization before the temperature cooled down to 230 °C (Fig. 5). This means β-form has almost no time to crystallize at high temperature, only α-form can crystallize as the temperature keeps on decreasing. That is the reason why only α-form crystal is obtained under quenching conditions. When the cooling rate is between 10 and 80 °C/min, there are different degrees of crystallization before the temperature is cooled down to 230 °C, but the sample does not have enough time to crystallize to the maximum crystallinity of sPS (Fig. 5). Under this condition, the α-form has a chance to crystallize at lower temperatures so that both form crystals coexist in the sample. And what is more, being calculated from WAXD, the amount of the β-form in samples crystallized at different cooling rates: 2, 5, 10, 20, 40 and 80 °C/min, is 100, 100, 100, 80, 25 and 0%, respectively. Meanwhile being obtained by non-isothermal crystallization with DSC measurement, the amount of the β-form in the samples at different cooling rates can draw almost the same conclusion. This precisely proves that β-form can only be obtained above about 230 °C, whereas the α-form can only be presented when the crystallization temperature is lower than about 230 °C.

In fact, there are some early papers [10,12,13,21,26,27] that have noticed the influence of crystallization temperature on the formation of the α and β-form crystals of sPS. Their results indicate at high enough crystallization temperature, only β-form was observed. With increasing cooling rate, the relative crystallinity of sPS reduced when the temperature cooled down to 230 °C. This can explain the observation of De Rosa et al. [12], where the amount of the α-form increases with increasing cooling rate.

As the crystallization kinetics of sPS largely depends on their molecular structures (molecular weight, branching degree, etc.), the crystallization kinetics of α- and β-form crystals should change with the different molecular structures. So the transition temperature (the formation of the α- and β-form crystals) of sPS (say 230 °C here), must be shifted with the molecular structure factors. But there must be a temperature where the β-form can only be presented above this temperature and α-form can only be obtained below this temperature.

4. Conclusions

The influence of crystallization temperature on the formation of the α and β-form crystals of sPS has been investigated. The results of X-ray diffraction and non-isothermal crystallization experiments indicate that the cooling rate from the melt should not be the intrinsic factor controlling the formation of the α- and β-form crystals. And the crystallization temperature seems certainly to have a more important influence. The α-form can only be obtained when the crystallization temperature is lower than about 230 °C, whereas the β-form can only be obtained when the crystallization temperature is higher than about 230 °C.

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