Solid-State Structure of Thermally Crystallized Syndiotactic Polystyrene

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ABSTRACT: The solid-state structure of syndiotactic polystyrene (s-PS) after crystallization from the melt and the glassy state was examined by differential scanning calorimetry (DSC), density, and X-ray diffraction analysis. It was possible to prepare semicrystalline s-PS containing either the pure α- or the pure β-crystalline form by melt crystallizing s-PS from 280 or 330°C. The measurements confirmed the low density of both crystalline forms, which in the case of α-crystalline form was smaller and in the case of β-crystalline form was only slightly larger than the density of the glassy amorphous s-PS. An endeavor to introduce the crystalline phase in s-PS through cold crystallization at constant temperature above the glass transition resulted in a complex ordered phase. This ordered phase, depending on the crystallization temperature, contained the planar chain mesomorphic phase and the α-crystalline phase with a low degree of perfection (cold crystallization in the range 120–175°C) or a mixture of the α- and β-crystalline forms with a high degree of perfection (cold crystallization in the range 210–260°C). The combination of DSC and X-ray measurements enabled us to resolve the complex ordered structure in semicrystalline s-PS after cold crystallization. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2705–2715, 2002

Key words: syndiotactic polystyrene (s-PS); crystallization; polymorphism

INTRODUCTION

Since it was first synthesized in the 1980s, syndiotactic polystyrene (s-PS) generated a strong practical and research interest because of its impressive material properties and unusual polymorphism of the solid-state structure. The solid-state structure of s-PS is very unusual and several polymorphic crystalline forms and the mesomorphic form were observed. Four main polymorphic crystalline structures were assigned

by Guerra et al., as α, β, γ, and δ.[1] These various crystalline forms differ by the conformation order and by the mode of crystalline packing of chains having the same conformation order. Two solvent-induced crystalline forms γ and δ forms contain helical chains with conformation order TTGG and identity period $c = 7.8$ Å. Thermal crystallization results in either α- or β-crystalline forms. Both α- or β-crystalline forms exhibit planar zigzag chain conformation order (TTTT) with identity period $c = 5.1$ Å. Figure 1(a–c) shows models of α- and β-crystalline forms drawn to scale. Carbon and hydrogen atoms are also drawn according to their van der Waals radii.

The structure of the β-crystalline form, first proposed by Chatani et al., is shown in Figure 1(a).[2] This crystalline form is distinguished by
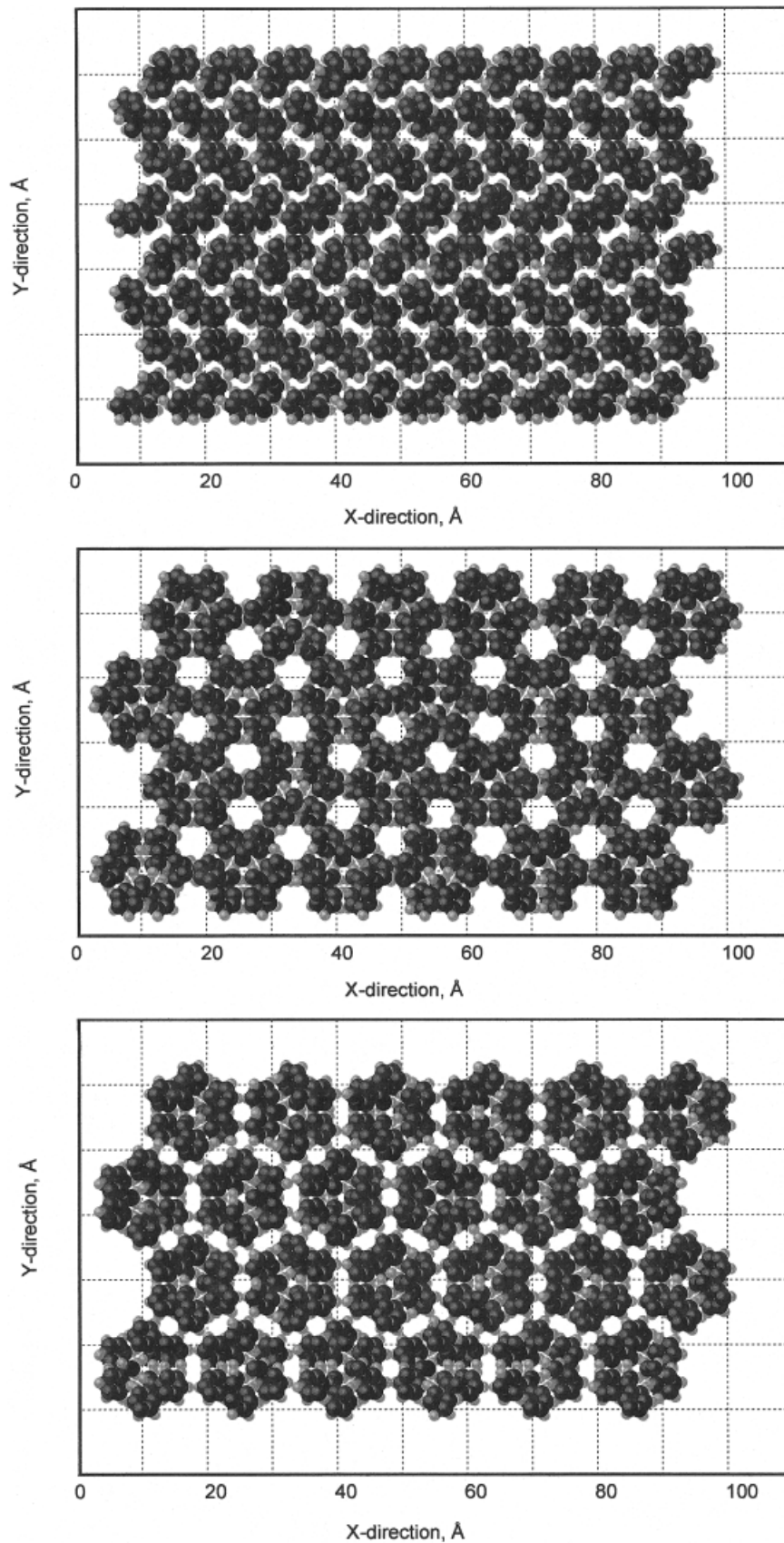
Figure 1 Scale models of β- and α-crystalline forms of s-PS: (a) β-crystalline form; (b) α-crystalline form (by Greis); (c) α-crystalline form (De Rosa).

orthorhombic chain packing with unit cell dimensions $a = 8.81$ Å, $b = 28.82$ Å, and $c = 5.1$ Å. The crystalline density of the β-crystalline form, 1.068 g/cm^3, calculated from the parameters of the unit cell, is quite loose, and it is only slightly larger than the density of the amorphous s-PS, 1.045 g/cm^3.[3] In the α-crystalline form, first the chains are packed in the clusters (triplets), each containing three chains. The backbones of these three chains make a core of the triplet, whereas the phenyl rings are pointed toward the periphery. Three triplets (nine chains) are included in a trigonal unit cell with unit cell dimensions $a = b = 26.26$ Å, $c = 5.1$ Å. Two possible models of chain packing in the α-crystalline phase are shown in Figure 1(b,c). Greis et al. proposed a packing model in which three triplets are considered at the same height with two identically positioned triplets and one rotated by 180°C [Fig. 1(b)].[4] DeRosa et al. proposed that the triplets have a relative shift $c/3$ along c-axis and rotated by 30° relative to azimuthal position of the triplets in the Greis model [Fig. 1(c)].[5] Despite the differences, both models predict the same density of the α form, 1.033 g/cm^3, which is smaller than the density of the amorphous phase as in the case with P4MP1. Two structural models predict different distribution of an unoccupied space in crystalline s-PS, which is responsible for the low density of the α crystals. In the Greis model [Fig. 1(b)], the structure exhibits large channels. Six channels, adjacent to the sides of each triplet, have almost circular aperture about 5 Å in diameter. In the De Rosa model of the α form, the unoccupied space almost uniformly surrounds each triplet in the form of a hollow cylinder with a thickness about 3–4 Å.

Crystalline s-PS demonstrates a variety of various crystalline forms. Depending on crystallization conditions, both pure α- and β-crystalline forms as well as their mixture could be found when s-PS is crystallized from the melt state.[1,6] When s-PS is cold crystallized above its glass transition temperature, the structure, in addition to the crystalline phase, contains the mesomorphic phase, which is characterized by the conformational order with lack of or very poorly developed structural order.[7,8,9] Complex ordered structure containing several crystalline phases and the mesomorphic phase pose a question of how to distinguish these different phases and measure their fractions.

EXPERIMENTAL

Sample Preparation

s-PS with an average molecular weight $M_w \approx$ 300,000 g/mol and polydispersity $M_w/M_n \approx 2$ was generously supplied in pellet form by the Dow Chemical Co., Midland, MI. Specimens, in the form of 165×165-mm-wide and 1-mm-thick rectangular plaques, were prepared by compression molding of melted pellets directly between two polished steel platens. The platens were placed in a press and preheated at a selected mold temperature for 15 min without pressure. Then, the pressure was increased to 30,000 psi and released; this cycle was repeated two times to ensure that the plaques would be free of bubbles. Finally, the platens were held at 30,000 psi for 15 min and either quenched to ice water to prepare the amorphous samples or cooled in the press to prepare the melt-crystallized samples. To prepare the amorphous samples, plaques were molded at 315°C. Two other mold temperatures were also chosen to prepare samples containing either predominantly α- or β-crystalline form. Low, 280°C, mold temperature was chosen to prepare samples containing α-crystalline form, and high, 330°C, mold temperature was used to prepare samples containing β-crystalline form. It was shown elsewhere that molding at low temperature facilitated the predominant formation of the α-crystalline form, whereas molding at high temperature facilitated the formation of the β form.[6,8] Samples, molded at 330°C, were left out in the hot press, after turning the electric power off, to allow the system to cool to room temperature overnight. It was imperative for the predominant formation of the β form to cool samples slowly. The cooling rate in the temperature range of crystallization was approximately 0.5°C/min. Three different cooling regimes were considered to prepare samples containing the α-crystalline form with an objective to vary the degree of crystallinity. The crystallization rate was shown to be an unimportant factor for the predominant formation of the α-crystalline form. Molded at 280°C, samples were cooled quickly by running cold water in the press. The cooling rate in this case was approximately 10°C/min. Samples were cooled slowly by turning the electrical power off, as in the case of samples prepared by melt crystallization from 330°C. We also developed the regime when samples were cooled very slowly by lowering temperature 1°C every 10 min (steplike cooling regime).

During the molding and crystallization procedure, the press was covered with temperature-resistant cloth, and nitrogen purge was arranged inside the cover to prevent samples from degrading at high temperature. For cold crystallization, sealed in the aluminum foil, amorphous plaques of s-PS were annealed in the oil bath for 1 h at a constant temperature in the range 120–260°C.

Characterization Techniques

Several methods were used to characterize the solid-state structure. Density was measured by using a gradient column constructed from liquid solution of diethylene glycol/ethylene glycol in accordance with ASTM-D 1505 Method B. The column was calibrated with glass floats of known density. Small pieces (~ 25 mm^2) were placed in the column and allowed to equilibrate for 15 min before the measurements were taken. The experimental error of the density measurements did not exceed ± 0.001 g/cm^3. The crystallinity from density was calculated only for melt-crystallized samples by using a simple two-phase model with constant density of amorphous phase, 1.045 g/cm^3, and constant densities of crystalline phases, 1.033 g/cm^3, for the α form, and 1.068 g/cm^3 for the β form. Volume and weight fractions of crystallinity measured in semicrystalline s-PS within experimental error were the same because of the very small difference between the densities of amorphous and pure crystalline phases. The differential scanning calorimetry (DSC) experiments were carried out by using a Rheometrics Scientific DSC Plus. The instrument was calibrated with indium, tin, lead, and sapphire standards. Heating scans were recorded at 10°C/min over the temperature range 30–320°C. Crystallinity from DSC data was calculated by using a heat of fusion of the perfect crystal, 53.2 J/g.[10] Wide-angle X-ray scattering measurements were conducted with automatic powder diffractometer Philips Model APD 3520 by using nickel-filtered Cu-Kα radiation (wavelength 1.542 Å). Powder samples were scanned within scattering angle range 2θ from 5 to 30° at 0.001°/min. The degree of crystallinity was calculated from intensities scattered by the crystalline and amorphous regions. The experimental peak intensities were corrected by using the Lorentz factor $L = 1/(\sin^2 \theta \cos \theta)$.
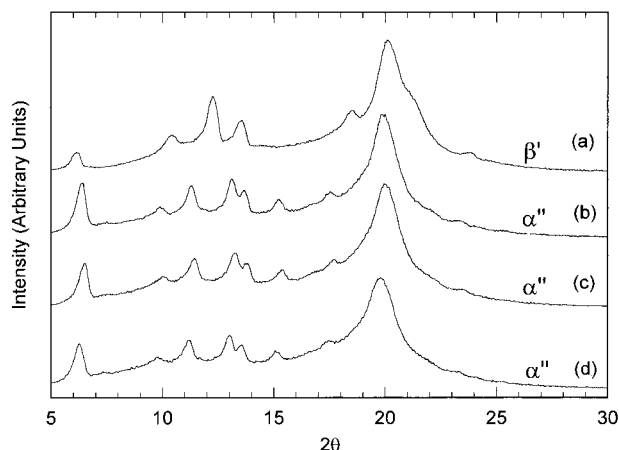

Figure 2 WAXS diffractograms of s-PS crystallized from melt state: (a) from 330°C; (b) from 280°C (very slow); (c) from 280°C (slow); (d) from 280°C (fast).

RESULTS AND DISCUSSION

Melt Crystallization

Figure 2 shows WAXS diffractograms of samples melt crystallized by cooling from 330 and 280°C. Samples crystallized from the melt by slow cooling from 330°C revealed the diffraction pattern typical of pure β-crystalline form. Moreover, the pattern suggested that this was limiting ordered modification, β', of the β form.[1,11] The diffractogram contained characteristic peaks at $2\theta =$ 6.2 (020), 10.4 (110), 12.2 (040), 13.6 (130), 18.6 (060), 20.2 (111), 21.3 (041), 23.9 (170), and 24.9° (080), which are generally attributed to the β form. The β form could exist in either limiting disordered modification β' or limiting ordered modification β''. When limiting ordered modification, β'', is formed, the diffractogram shows additional reflections located at $2\theta =$ 11.8 and 15.8°, which were absent in our case. The difference between β' and β'' modifications of the β-crystalline form can be understood in terms of stacking two kinds of macromolecular bilayers. These two bilayers have different orientation of lines connecting two adjacent phenyl rings. The ordered modification is distinguished by regular alternating of these two orientations [Fig. 1(a)], whereas in disordered modification, these orientations are alternated randomly. Limiting ordered modification, β'', is typically obtained when films of s-PS are prepared by casting from certain solvents at elevated temperatures.[1,2] The formation of the β' form is common when samples are crystallized directly from the melt.

All samples melt crystallized from 280°C fast, slow, or very slow (steplike cooling regime) exhibited similar diffraction pattern, typical for pure α-crystalline form, with peaks located at $2\theta = 6.7$ (110), 10.3 (210), 11.7 (300), 13.5 (220), 14.0 (310), 15.6 (400), 17.9 (410), 20.4 (211), 22.2 (510), and 23.8° (600). Peaks located at $2\theta = 6.7$, 11.7, 13.5, 17.9, 20.4, 22.2, and 23.8° are generally assigned to the α-crystalline form.[5] Three additional characteristic peaks located at $2\theta = 10.3$, 14, and 15.6° indicated that this was limiting ordered modification, α″, of the α form. These three peaks are absent in the case of limiting disordered modification, α′, of the α form. Limiting ordered modification, α″, according to De Rosa, shows an order in the positioning of the triplets [Fig. 1(c)] (e.g., considering any three adjacent triplets in the structure); one triplet always is oriented in one direction and the other two are rotated by 60° relative to the orientation of the first triplet. Although the orientation of one and the other two triplets are different, these two orientations are isosteric with respect to the orientation of the phenyl rings. The phenyl rings in each triplet are oriented in the same manner despite the triplet rotation. In the limiting disordered modification, α′, the distribution of the two isosteric orientations between triplets is random. In terms of the distribution of unoccupied space, limiting ordered and limiting disordered modifications must be identical. The formation of limiting ordered modification, α″, of the α form is typically associated with crystallization from the melt. In turn, cold crystallization from the glassy state typically results in the formation of limiting disordered modification, α′.[5,12]

Figure 3 shows DSC scans of samples crystallized from the melt state. Samples melt crystallized quickly and slowly from 280°C showed similar thermograms with single melting peak at about 270°C. Samples melt crystallized very slowly from 280°C (steplike regime) exhibited two melting peaks with maximums located at about 270 and 280°C. Low-temperature peak was larger and broader than the high-temperature peak. Samples melt crystallized from 330°C showed two melting peaks with the maxima located at 260 and 270°C. These peaks exhibited similar width; however, the low-temperature peak was smaller than the high-temperature peak. Melt-crystallized s-PS containing the α-crystalline phase usually shows a single melting peak with a maximum at about 270°C.[1,3] It was surprising to observe two melting peaks for s-PS after melt crystalliza-
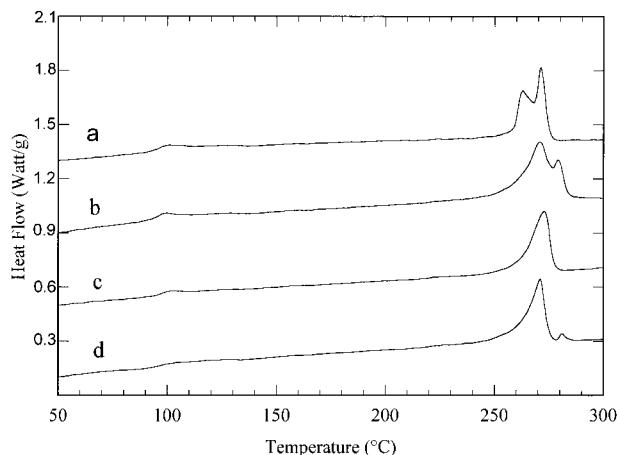

Figure 3 Melting thermograms of s-PS crystallized from melt state: (a) from 330°C; (b) from 280°C (very slow); (c) from 280°C (slow); (d) from 280°C (fast).

tion from 280°C using steplike cooling because this cooling regime also resulted in the α-crystalline form. In contrast, double-peak melting behavior for samples containing the β-crystalline form is very common.[3,11]

The interpretation of dual-peak melting behavior, which is frequently observed in semicrystalline polymers, has been a subject of controversy for the last 20 years.[13] Two different explanations of this phenomenon were proposed. The melting-recrystallization model explains two-peak melting, assuming that the low-temperature peak represents melting of kinetically the most favorable population of lamellae, associated with certain average lamellae thickness. This population is developed when samples are cooled from the melt. High-temperature peak represents the melting of thicker lamellae formed from the original lamellae during their partial melting and recrystallization during the DSC scan.[14,15] The dual lamellar thickness model explains double-endothermic behavior differently. It considers the concurrent formation of the two populations of thin and thick lamellae formed upon crystallization from the melt. The low-temperature melting peak is then associated with melting of thinner lamellae and the high-temperature melting peak is associated with melting of thicker lamellae.[16,17] There is strong evidence, presented elsewhere, based on the X-ray observations conducted during the temperature scan, the dependence of melting behavior on heating rate, that the dual-peak melting behavior for the β-crystalline form is in good agreement with the melting-recrystallization

Table I Densities and Crystallinities of Melt-Crystallized and Cold-Crystallized s-PS

Materials	Density (g/cm^3)	Density Crystallinity	DSC Crystallinity	X-ray Crystallinity	Fraction	
					α	β
Amorphous a-PS	1.046 ± 0.001	0	0	0	—	
Amorphous s-PS	1.045 ± 0.001	0	0	0	—	
s-PS melt-crystallized from 280°C (fast)	1.040 ± 0.001	0.42 ± 0.08	0.42 ± 0.04	0.27 ± 0.04	1	0
s-PS melt-crystallized from 280°C (slow)	1.040 ± 0.001	0.42 ± 0.08	0.44 ± 0.04	0.33 ± 0.05	1	0
s-PS melt-crystallized from 280°C (very slow)	1.040 ± 0.001	0.42 ± 0.08	0.47 ± 0.05	0.31 ± 0.05	1	0
s-PS melt-crystallized from 330°C (slow)	1.058 ± 0.001	0.57 ± 0.05	0.51 ± 0.05	0.37 ± 0.05	0	1
Cold-crystallized at 120°C	1.046 ± 0.001	—	0.23 ± 0.03	0	—	
Cold-crystallized at 130°C	1.046 ± 0.001	—	0.40 ± 0.04	0.12 ± 0.02	—	
Cold-crystallized at 140°C	1.044 ± 0.001	—	0.47 ± 0.04	0.16 ± 0.02	—	
Cold-crystallized at 150°C	1.044 ± 0.001	—	0.48 ± 0.04	0.20 ± 0.03	—	
Cold-crystallized at 160°C	1.046 ± 0.001	—	0.49 ± 0.04	0.23 ± 0.03	—	
Cold-crystallized at 175°C	1.047 ± 0.001	—	0.49 ± 0.04	0.24 ± 0.03	—	
Cold-crystallized at 210°C	1.046 ± 0.001	—	0.50 ± 0.04	0.27 ± 0.03	0.86	0.14
Cold-crystallized at 240°C	1.046 ± 0.001	—	0.49 ± 0.04	0.31 ± 0.04	0.80	0.20
Cold-crystallized at 260°C	1.046 ± 0.001	—	0.52 ± 0.04	0.33 ± 0.04	0.68	0.32

model.[1,3] In turn, the explanation of dual melting behavior of the α crystals formed upon steplike cooling regime, based on our observations, seems to be in better agreement with the dual lamellar thickness model. The low-temperature melting peak with the maximum at 270°C is associated with the melting of a large population of thinner lamellae formed within a narrow cooling temperature range, at about 260°C, upon cooling. Similar crystalline population is always present when samples of s-PS are cooled fast or moderately slow from 280°C. Melting of this crystalline population resulted in a single melting peak located at 270°C (Fig. 2). High-temperature peak with maximum at 280°C most likely is associated with the melting of a small population of thicker lamellae formed at higher than 260°C temperatures during this very slow cooling.

Table I reports densities and crystalline fractions of melt-crystallized samples determined by the X-ray, density, and DSC methods. We included in the table, in addition to the densities of semicrystalline s-PS, the densities of the amorphous syndiotactic and atactic polystyrene. The atactic polystyrene (a-PS), also supplied by the Dow Chemical Co., exhibited the molecular weight and polydispersity similar to the s-PS. It was interesting to compare the densities of these two amorphous polymers to understand whether the tacticity influenced the packing of polystyrene chains in the amorphous state. The measure-

ments showed that the densities of amorphous s-PS and a-PS were identical within reported experimental error. Therefore, tacticity had no effect on density and, subsequently, on overall packing of polystyrene chains in the amorphous state. A similar conclusion was drawn elsewhere after comparing the densities of amorphous atactic and isotactic polystyrenes.[18]

Semicrystalline s-PS containing the α-crystalline form exhibited smaller density and semicrystalline s-PS containing the β-crystalline form exhibited larger density than the density of amorphous s-PS. The crystalline fractions determined by using DSC and density methods agreed reasonably well. Reasonable agreement between the crystalline fractions as determined by DSC and density measurements indicated that partially crystallized from the melt s-PS obeyed a two-phase model. This fact was consistent with the flexible nature of chain backbone in s-PS. An agreement between crystallinities determined by DSC and density methods confirmed that it was reasonable to use the same heat of fusion for the perfect crystal, 53.2 J/g, to calculate the crystallinity in s-PS containing either α- or β-crystalline forms. In fact, it is not very clear why very different crystalline structures such α and β forms exhibit very similar heat of fusion for the perfect crystal. We found that the X-ray crystalline fractions were notably lower than those obtained by DSC and density. Average difference between
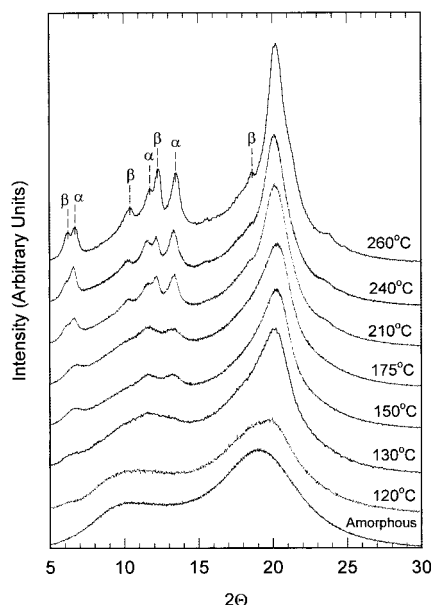
Figure 4 WAXS diffractograms of s-PS cold crystallized from glassy state at different temperatures.

DSC and X-ray crystalline fractions for melt-crystallized s-PS was practically constant, 0.14 ± 0.02. Smaller crystalline fractions, as determined by X ray, indicated that the X ray was probably less sensitive than the DSC and density methods to detect crystals which are too small to produce the discrete X-ray reflections. A similar kind discrepancy was reported for semicrystalline isotactic polystyrene.[18]

Cold Crystallization

Figure 4 shows WAXS diffractograms of s-PS cold crystallized for 1 h at various temperatures. The figure also shows the diffractogram for an amorphous sample. Amorphous samples exhibited a broad halo consisting of two broad overlapping peaks with maxima at $2\theta = 9.3°$ and $2\theta = 19.4°$. Two-peak amorphous halo is a characteristic feature of amorphous PS and its origin was discussed elsewhere.[19] Samples annealed at 120°C exhibited the diffraction pattern, which was practically indistinguishable from the amorphous halo. Annealing at 130°C, a temperature within cold-crystallization range of s-PS, resulted in some distinguishable changes in the form of X-ray diffractogram compared to that for amorphous sample. The diffractogram revealed practically the same two-peak feature typical of the amorphous halo. However, the peak maximums shifted toward the larger scattering angles and the main

amorphous halo peak significantly sharpened. Annealing in the range 140–175°C showed the appearance and sharpening of three broad reflections located at $2\theta = 6.7°(110)$, $11.7°(300)$, and $13.5°(220)$ associated with the formation of the α' limiting ordered modification of the α form. The sharpening of these reflections indicated the transformation of crystals with lower degree of perfection toward higher degree of perfection. The α crystals were fully formed only after annealing at 210°C. Above 210°C, the sharpness of the characteristic reflections, assigned to the α-crystalline form, remained practically unchanged. Starting at 210°C, several new reflections located at $2\theta = 6.2(020)$, $10.4(110)$, $12.2(040)$, $18.6(060)$, $23.9°(170)$ appeared in the diffractogram. These reflections were assigned to the β-crystalline form (Fig. 2). Therefore, cold crystallization at higher temperatures resulted in the formation of a mixture of α- and β-crystalline forms. At higher temperatures, the intensities of the reflections associated with the β-crystalline form increased in comparison with the reflections associated with the α form, indicating the growth of β-crystalline fraction in the mixture.

The fractions of two crystalline forms were evaluated by using the method proposed by Guerra et al.[1] According to this method, two overlapping peaks at $2\theta = 11.7°$ (associated with the α form) and at $2\theta = 12.2°$ (associated with the β form) were considered in the diffractogram. The deconvolution of these two peaks for the samples cold crystallized at 210, 240, and 260°C is shown in Figure 5(a–c). After peak deconvolution, the areas of the two peaks, $A(11.6°)$ and $A(12.2°)$, were measured and the relative fraction of the α form in the total X-ray crystalline fraction was calculated according to the empirical formula:

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

The fractions of α- and β-crystalline forms in the total crystallinity are reported in Table I. Although after cold crystallization at 210°C the relative fraction of the β form was only 0.14, after cold crystallization at 260°C this fraction was already rather significant, 0.32.

The concurrent formation of α and β crystals is common when s-PS is crystallized from the melt at certain conditions, usually associated with relatively high temperature of the melt and moderate cooling rates.[1] Cold crystallization is normally
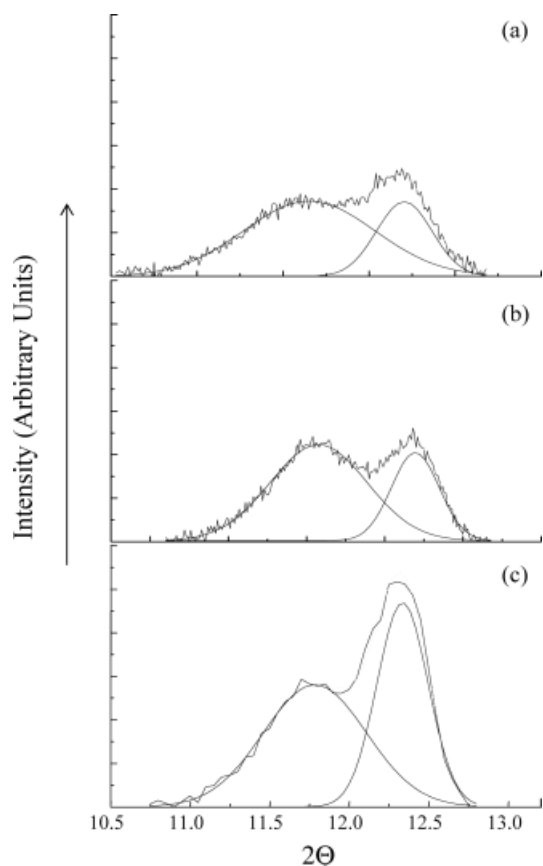
Figure 5 Deconvolution of two characteristic X-ray peaks of α ($2\Theta = 11.7°$) and β ($2\Theta = 12.2°$) of s-PS cold crystallized at (a) 210°C; (b) 240°C; (c) 260°C.

associated with the formation of the mesomorphic phase or α-crystalline form. The concurrent formation of α- and β-crystalline forms upon cold crystallization is unusual. This unusual behavior was attributed to an abrupt heating of amorphous s-PS in the oil bath. Abrupt heating prevented amorphous s-PS from rapid filling of the structure of s-PS with kinetically more favorable α-crystalline form at large supercoolings. When the temperature was already high, the rates of the formation of both crystalline forms were comparable, and the mixture of α and β crystals was developed in semicrystalline s-PS.

Figure 6 shows DSC thermograms of amorphous samples cold crystallized 1 h at various temperatures above glass transition temperature. Amorphous samples exhibited glass transition at about 95°C, followed by cold-crystallization peak with onset at 130°C and maximum at 151°C, and a melting peak with maximum at 270°C. Samples cold crystallized at 120°C also exhibited a cold-crystallization peak. However, this peak was substantially smaller in comparison with that for the amorphous polymer. This result clearly indicated that a significant amount of amorphous material was already transformed into crystalline phase even at this low annealing temperature below cold-crystallization temperature region. In contrast to DSC, the corresponding X-ray diffractogram for samples annealed at 120°C (Fig. 4) did not show the presence of crystallinity.
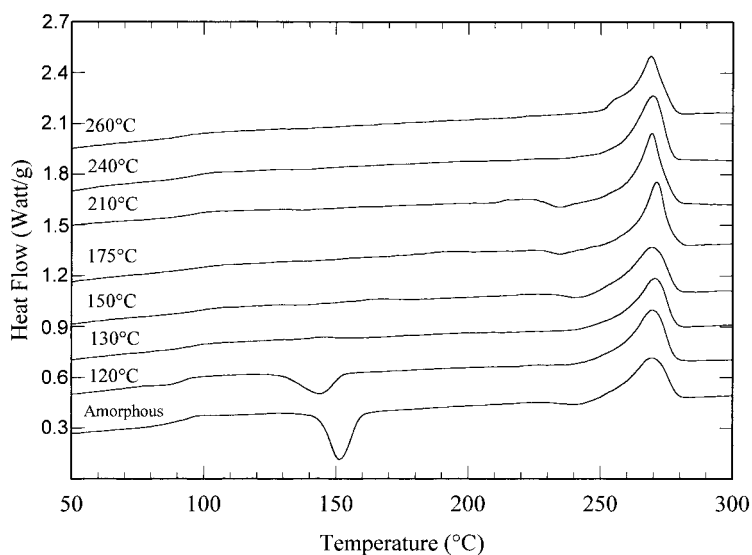

Figure 6 Melting thermograms of s-PS cold crystallized from glassy state at different temperatures.

The inability of X ray, in comparison with other techniques, to detect a large amount of crystalline phase in s-PS, especially when it was formed upon annealing at low temperatures, was recognized first by DeCandia et al. and related to the formation of the mesomorphic phase associated with the conformational order inside the chains (plane chain zigzag) and with paracrystalline disorder between the chains.[7] More recently, the detailed structural analysis of mesomorphic structure was conducted by Auriemma et al. by using X-ray diffraction and FTIR. They concluded that the mesomorphic phase consists of triplets of polystyrene chains, rather than randomly spaced chains with conformational order as it was originally thought, with complete order inside the triplets and paracrystalline disorder between the triplets.[8]

Samples cold crystallized in the temperature range 130–150°C showed very similar thermograms. The thermograms contained only broad melting peak with maximum at 270°C. There were no cold-crystallization peaks in the thermograms. The ordered phase reached its maximum value after annealing for 1 h above 120°C. The melting peak became narrow after cold crystallization in the range 175–210°C. However, it broadened again after annealing at 240°C. After annealing at 260°C, an additional low-temperature melting peak with a maximum located at about 260°C became apparent in the thermograms. This peak was due to the melting of the β crystals formed upon annealing at higher temperatures.

Table I also presents densities and volume crystallinities determined by X ray and DSC for cold-crystallized samples. The table shows the relative fractions of α- and β-crystalline forms for samples cold crystallized at 210–260°C. All cold-crystallized samples exhibited virtually the same density as amorphous s-PS, 1.045 ± 0.001 g/cm^3. Therefore, the density method was not used to calculate the crystallinity because cold-crystallized s-PS did not obey the two-phase model in contrast with melt-crystallized s-PS. The structure of s-PS after cold crystallization contained a complicated mixture of various ordered forms. After cold crystallization at low temperatures, the structure of s-PS contained the amorphous phase and the mesomorphic phase along with the α crystals with a low degree of perfection. Most likely, the mesomorphic phase and the α crystals with a low degree of perfection exhibited density similar to the density of pure amorphous phase. This can then explain the constant density of s-PS after cold crystallization at low temperatures. After
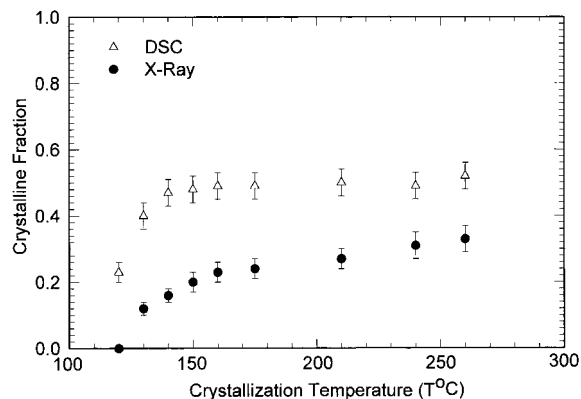

Figure 7 Crystalline fractions of cold-crystallized samples measured by DSC and X ray as a function of cold-crystallization temperature.

cold crystallization at higher temperatures (210–260°C), the structure of s-PS contained the amorphous phase and α along with β crystals all with a high degree of perfection. In this case, the overall density was also constant, however, mainly because of the compensation effect resulted from the lower than amorphous density of the α-crystalline phase and larger than amorphous density of the β phase. The density of semicrystalline s-PS estimated from fractions of α form and β forms in the mixture showed fairly reasonable agreement with the experimental density.

Figure 7 shows the crystalline fractions measured by DSC and X ray as a function of cold-crystallization temperature. Cold-crystallized samples showed a very strong discrepancy in the amount of crystallinity measured by DSC and X ray, especially when cold crystallization was carried out at low temperatures of 120–175°C. The maximum difference was up to 0.3. After cold crystallization at 120°C, the DSC showed a significant amount of crystalline fraction, 0.23, as the X-ray method showed no indication of crystalline phase. Both techniques revealed a rapid increase of crystallinity within a very narrow range of crystallization temperatures 130–140°C. After cold crystallization at 150°C, the DSC crystalline fraction reached the maximum at about 0.50. The X-ray crystallinity continued to grow slowly after 150°C. However, starting at 210–240°C, the difference between the DSC and X-ray crystalline fractions was found to be close to that found for melt-crystallized samples, which was explained earlier that X ray was probably not sensitive enough to detect small crystals. Therefore, after cold crystallization at high temperatures, above

210°C, the ordered structure contained no mesomorphic phase and ordered phase presumably contained a mixture of α and β crystals with a high degree of perfection.

Relatively large discrepancy between crystalline fractions determined by the DSC and X-ray methods found after cold crystallization of s-PS at low-crystallization temperatures could be understood assuming that the DSC measures the total amount of ordered phase in the cold-crystallized samples of s-PS, including the mesomorphic phase and the crystalline phase with different degree of perfection, small crystals, and so on. In turn, the X ray measures only the amount of crystalline phase, and, apparently, it is more sensitive to the crystalline phase with a high degree of perfection and larger size crystals. The sensitivity of the DSC to measure all forms of the ordered phase is brought about by the fact that the constituents with low degree of perfection or structural order constantly undergo a series of the consecutive melting-recrystallization events during the DSC heating scan toward crystalline phase with high degree of perfection. At the end of this melting-recrystallization chain, they all become a part of relatively uniform crystalline population with high degree of perfection and melt upon the DSC heating run at about 270°C. Therefore, the area under the final melting peak (in our case, except for s-PS cold crystallized at 120°C) defines the total amount of ordered phase formed in the polymer after cold crystallization. These melting-recrystallization processes probably are associated with very small change of enthalpy, and the corresponding DSC thermograms show practically no changes between the glass transition and the melting region despite the continuous changes of the solid-state structure of s-PS in the course of the DSC scan (Fig. 6). The DSC measurements suggest that the amount of ordered phase gets to saturation already after cold crystallization at 140°C. Above 140°C, the amount of ordered phase does not change, and only the redistribution of the amount of mesomorphic phase and the amount of α-crystalline phase with low-degree perfection takes place with an increase in cold-crystallization temperature.

The changes of the s-PS solid-state structure upon heating in the DSC scan can be observed using X ray. The following experiment was conducted. The amorphous plaque was annealed for 1 h at 130°C. Then, several small pieces of the annealed plaque were heated in the DSC pan to the selected temperatures 150, 175, 210, and 240°C at 10°/min and rapidly cooled to room temperature. The X-ray diffractograms for these thermally treated samples
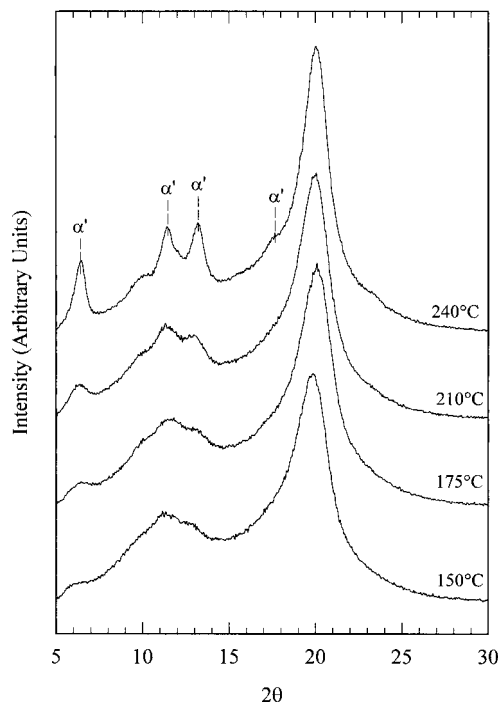

Figure 8 WAXS diffractograms of s-PS cold-crystallized at 130°C and then heated at 10°/min to different temperatures.

are shown in Figure 8. The progression of the ordered structure with the selected temperature toward the α'-crystalline form with higher degree of perfection is evident. It is interesting to note that, in contrast to annealing in the oil bath, which results in the mixture of α and β crystals, slow heating produced only the α'-crystalline form.

CONCLUSION

Crystalline s-PS showed complex solid-state structure, which was strongly dependent on the crystallization conditions. Melt crystallization from 280°C led to the formation of only α''-crystalline form. Melt crystallization from 330°C led to the formation of only β'-crystalline form. Melt-crystallized samples obeyed the two-phase model consisting of the amorphous and the corresponding crystalline phases. The measurements confirmed the low density of both crystalline forms, which in the case of α-crystalline form was smaller and in the case of β-crystalline form was only slightly larger than the density of the glassy amorphous s-PS.

Cold crystallization led to the formation of complex ordered phase. Cold crystallization at low

temperatures (120–175°C) led to the formation of the planar mesomorphic phase and α'-crystalline phase with low degree of perfection. Crystallization at higher temperatures (210–260°C) in the oil bath led to the formation of a mixture of α'-crystalline phase and β'-crystalline phase with high degree of perfection. Cold-crystallized s-PS did not obey the two-phase model. It was shown that the total amount of ordered phase, consisting of the mesomorphic phase and the α'-crystalline phase with low degree of perfection, could be determined by the DSC, whereas the X ray is only able to measure the amount of crystalline phase. A combination of both techniques seems to be very important to resolve and analyze this complex solid-state structure.

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