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Crystallization from the melt of α and β forms of syndiotactic polystyrene

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Abstract

The crystallization of *trans*-planar α and β forms of syndiotactic polystyrene is studied through X-ray diffraction and DSC analyses of melt-crystallized samples. The factors controlling the crystallization of the two forms are analyzed. Pure α and β forms of syndiotactic polystyrene can be easily obtained setting the maximum temperature at which the melt is heated and the permanence time of the melt at this temperature. The crystallization of the α and β forms does not depend on the crystallization temperature, at least in the range of accessible crystallization temperatures, between 240 and 270 °C, but only depends on the presence of the 'memory' of the α form in the melt. The most important factors are, indeed, the crystalline form of the starting material used in the melt crystallization experiments and the maximum temperature of the melt. Relevant recrystallization phenomena, occurring during the melting of the samples crystallized from the melt at low crystallization temperatures, are responsible for the complex melting behavior of the α and β forms. The recrystallization involves only lamellar thickening of the crystals of the same form (α or β) and not structural transformation.

Keywords: Syndiotactic polystyrene; Melt-crystallization; α and β Forms

1. Introduction

Syndiotactic polystyrene (s-PS) presents a complex polymorphism [1–17]: four different crystalline forms α [5,6,10], β [7–9], γ [4] and δ [11–13], two mesomorphic forms [12,14,15] and various clathrates forms [16–18] have been found so far. The most stable α and β forms are characterized by chains in *trans* planar conformation, they are obtained by melt crystallization procedures and present high melting temperatures (≈270 °C). γ and δ forms, as well as all the clathrate forms are characterized by chains in s(2/1)2 helical conformation. They are thermally unstable, δ form and clathrate samples transform into γ form by annealing at 130 °C and into α form by annealing at higher temperatures (180 °C) [4,12,13].

The polymorphism of s-PS is further complicated by the presence of structural disorder in both α and β forms [4–8]. The crystal structures of α and β forms are, indeed, described in terms of disordered modifications intermediate between limit disordered models (α′ and β′) and limit ordered models (α″ and β″) [5–8]. In particular, melt crystallization procedures generally produce crystalline modifications of the α and β forms close to the limit ordered α″ and limit disordered β′ models, respectively [4]. Crystalline modifications close to the limit disordered α′ model are obtained by annealing amorphous s-PS samples or samples in the crystalline γ form [4–6], whereas crystalline modifications close to the limit ordered β″ model are obtained by crystallization from solutions, when the solvent is rapidly removed at high temperatures (> 150 °C) [8].

The crystallization of the α and β forms strongly depends on the experimental conditions. It has been reported that, in the case of the crystallization from the melt, the most important factors are the maximum temperature at which the melt is heated, the permanence time of the melt at that temperature, the crystallization temperature, the cooling rate and the crystalline form of the starting material [4,19].

Recently, many papers have appeared in the literature concerning the crystallization of α and β forms in s-PS homopolymer and its blends [4,19–35]. Guerra et al. [4] in their pioneer work have reported that for moderate cooling rates from the melt the crystalline form present in the samples is essentially related to the thermal history of the melt. In particular, a pure β form is obtained from the melt only if no memory of the crystals of α form remains in the melt, e.g. when the melt is heated at high temperature and kept at that temperature for long time. Crystals of α form are

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instead obtained in the presence of the memory of α form in the melt, that is when the melt is heated at temperatures relatively low (e.g. 10 °C above the melting temperature) [4]. Moreover, Guerra and De Rosa in Refs. [4,8,32] have shown that α form crystals are obtained by fast cooling from the melt [4,8] and by cold crystallization from the quenched amorphous glass [4,32]. More recently, the effects of most of these parameters, in particular the maximum temperature of the melt, the cooling rate to the crystallization temperature, the crystallization temperature and the crystallization time have been extensively studied by Woo et al. [19,21–26]. The results are similar to those already found in the earlier studies of Refs. [4,5,8,31,32]. In summary, the crystallization of α form is basically favored under three conditions: (i) fast cooling to room temperature from the melt [4,8,23]; (ii) melt crystallization at low temperatures (lower than 230 °C) [21–23] and (iii) cold crystallization from the quenched glass [4,22,26,32]. In particular, the crystallization from the melt at temperatures higher than 260 °C favors the formation of the β form, whereas at crystallization temperatures lower than 230 °C the α form is obtained [21–28]. Upon melt crystallizations at most accessible temperatures, between 230 and 260 °C, it has been reported that mixtures of crystals of α and β forms are obtained [23]. Under conditions approaching equilibrium only the β form is generally present. These data have indicated that the crystallization of α form is, in general, the result of a kinetically controlled process, the β form being the thermodynamically stable form.

Woo et al. have also studied the crystallization of α and β forms in terms of the classical metastability of the crystal structures and the morphological metastability concerning lamellar size [25]. Since the latter changes with the crystallization temperature, the relative stability of polymorphic forms may also change, when, for instance, a stable phase becomes metastable because the lamellar dimensions of the competing phase are differently influenced by the crystallization temperature [36]. This phase stability inversion with lamellar size allowed interpreting the solid–solid transition from α to β form found by Woo et al. during the isothermal melt crystallization [25].

More recently, the effect of the cooling rate and the crystallization temperature in non-isothermal crystallization experiments has been analyzed [27,28]. It has been suggested that the cooling rate from the melt is not the intrinsic factor controlling the formation of α and β forms, whereas the crystallization temperature has a more important influence [28]. According to this hypothesis, the crystallization of the α form by fast cooling from the melt, found in the earlier study [4,8], is interpreted as a crystallization at temperatures below 230 °C where the α form is favored. During the fast cooling the β form, which crystallizes at higher temperatures, has no time to crystallize and only the α form can crystallize as the temperature decreases [28].

Even though most of the factors controlling the crystallization of α and β forms has been clarified, the relationship between the memory effect of the α form in the melt and the crystallization temperature have not been investigated in detail.

In this paper a detailed study of the polymorphic behavior of s-PS samples crystallized from the melt in isothermal and non-isothermal conditions is presented with the aim to clarify the influence of the crystallization temperature in the presence or not of the memory effect. The crystalline form of the starting material, the crystallization temperature, the maximum temperature of the melt and the permanence time of the melt at this temperature have been analyzed.

Controlling of conditions to obtain pure α and β forms is of particular interest especially in consideration of their different physical properties. In fact, s-PS samples in the crystalline α form, as well as in γ and δ forms and amorphous samples, transform into clathrate samples by swelling with suitable solvents, whereas this transition never occurs for samples in the crystalline β form [37,38]. Hence, the s-PS β form could represent a thermoplastic polymeric material of potential industrial interest due to its very high melting point, fast crystallization rate, good chemical and thermal resistance and excellent processability in most thermoplastic fabrication technologies.

2. Experimental section

s-PS was supplied by the Dow Chemical Company. The polymer is highly stereoregular, with $[rr] = 98\%$; the weight-average molecular weight and the polydispersity index, determined via gel permeation chromatography are $M_w = 3.17 \times 10^5$ g/mol and $M_w/M_n = 3.91$, respectively.

The non-isothermal melt crystallizations were carried out in a molding press. The polymer pellets in the amorphous phase were introduced between the plates of the press, previously heated up the maximum temperature (T_{max}), kept at that temperature for a given time (t_{max}) and cooled to room temperature at a rate of about 10 °C/min.

The isothermal melt crystallization were performed in a Perkin–Elmer DSC-7 calorimeter in flowing nitrogen atmosphere. s-PS samples, in a given crystalline modification (α, β or a mixture of α and β forms) were put in the DSC pan, heated up to T_{max}, kept at that temperature for t_{max}; they were then rapidly quenched to the crystallization temperature T_c and kept at this temperature for a time t_c long enough to allow complete crystallization at T_c. The samples were then rapidly cooled to room temperature and analyzed by X-ray diffraction and DSC. In the various isothermal crystallizations, the crystallization time t_c is different depending on the crystallization temperature. The shortest time is 24 h for the lowest crystallization temperature and increases with increasing crystallization temperature.

The X-ray diffraction patterns were obtained at room temperature with an automatic Philips powder diffractometer using Ni filtered Cu Kα radiation, and at higher temperatures using an attached Anton Paar TTK camera. The X-ray diffraction profiles were recorded in the 2ϑ range 4–40° at a scan rate of 0.01 °(2ϑ)/s.

The DSC measurements were performed with a differential scanning calorimeter (DSC) Perkin–Elmer DSC-7 with scans at heating rates of 2.5, 10, and 20 °C/min in a flowing nitrogen atmosphere.

3. Results and discussions

Non-isothermal melt crystallization. The X-ray powder diffraction profiles of s-PS samples crystallized from the melt, by cooling to room temperature the melt heated at different $T_{\max}$ values, in the range 280–320 °C, and for $t_{\max} = 5$ min are shown in Fig. 1. The sample crystallized from $T_{\max} = 280$ °C, (curve a of Fig. 1) is basically in the α form, as indicated by the presence of reflections at $2\vartheta = 6.8°$ and 11.8°, typical of the α form and by the absence of the reflection at $2\vartheta = 6.2°$ and the low intensity of that at 12.3°, typical of the β form [4]. For higher $T_{\max}$ values the β form crystallizes and mixtures of α and β crystals are obtained, as indicated by the appearance of the reflections at $2\vartheta = 6.2°$ and 12.3° in the X-ray diffraction profiles b–d of Fig. 1. With increasing $T_{\max}$, the amount of β form in the crystalline phase increases, whereas that of α form decreases, as shown by the increase in the intensities of the diffraction peaks typical of β form at $2\vartheta = 6.2°$ and 12.3° and the decrease in those of the reflections at $2\vartheta = 6.8°$ and 11.8° of α form. For $T_{\max} = 320$ °C the sample crystallizes in the pure β form (curve e of Fig. 1).

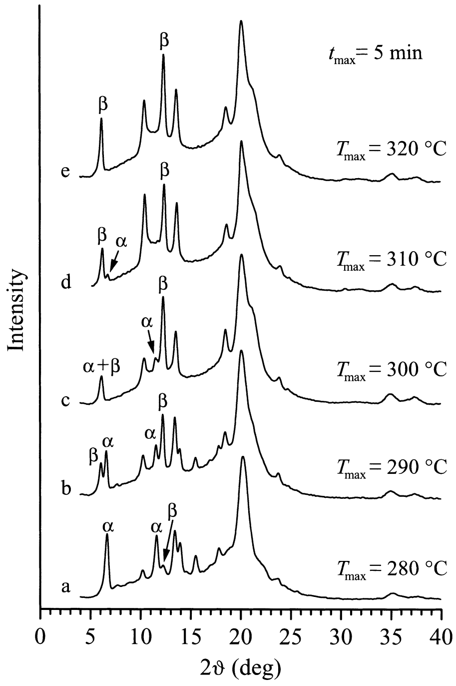

Fig. 1. X-ray powder diffraction profiles of s-PS samples crystallized from the melt by cooling to room temperature the melt heated at the indicated $T_{\max}$ temperatures and for $t_{\max} = 5$ min. The cooling rate is always ~10 °C/min. The reflections typical of the α and β forms are indicated.

The crystallization of α and β forms depends also on the permanence time of the melt at the temperature $T_{\max}$. The X-ray diffraction profiles of s-PS samples crystallized from the melt for different $t_{\max}$ and for $T_{\max} = 280$, 290, and 320 °C are shown in Fig. 2(A)–(C), respectively. For relatively low $T_{\max}$ values (<300 °C), with increasing the permanence time of the melt at $T_{\max}$, the portion of the sample crystallized in the β form increases, as indicated by the progressive increase in the intensities of the reflections of the β form ($2\vartheta = 6.2°$ and 12.3°) and the decrease in those of the reflections of the α form ($2\vartheta = 6.8°$ and 11.8°) in Fig. 2(A) and (B). For higher values of $T_{\max}$ melt crystallized s-PS samples are always in the pure β form, regardless of the permanence time of the melt at that temperature (Fig. 2(C)).

These data indicate that the crystalline α form is favored for low $T_{\max}$ and $t_{\max}$ values (e.g. $T_{\max} \leq 280$ °C, $t_{\max} \leq 5$ min), whereas the β form is obtained when the melt is heated at higher temperature (e.g. $T_{\max} \geq 320$ °C) and for long values of $t_{\max}$.

These results are in agreement with those shown in Ref. [4] and have been interpreted by assuming the presence in the melt of a memory of crystals of α form. When a memory of α form is still present in the melt, for instance for low $T_{\max}$ and $t_{\max}$ values, the crystallization of the α form is favored; when this memory is erased, for instance by heating the melt at high temperature, at least 50 °C above the melting point of the starting material, the β form is always obtained.

It is worth noting that the crystalline modifications of the α form obtained in melt crystallized s-PS samples are close to the limit ordered model α″, whereas those of the β form are similar to the limit disordered model β′. This is evident by the presence of the reflections at $2\vartheta = 10.3°$, 14° and 15.6° (marked with asterisks in Fig. 2(A)), diagnostic of the limit ordered modification α″, in the X-ray diffraction profiles a and *b* of Fig. 2(A), and by the absence of the reflections at $2\vartheta = 11.8°$ and 15.9°, typical of the limit ordered modification β″ in the profiles of Fig. 2(C) [4].

Isothermal melt crystallization. Samples of s-PS have been isothermally crystallized from the melt at different crystallization temperature T_c, starting from material in the pure α and β forms, as well as crystallized in mixtures of α and β forms. Moreover, the crystallizations have been performed varying the maximum temperature at which the melt is heated ($T_{\max}$) and the permanence time of the melt at this temperature ($t_{\max}$). The accessible crystallization temperatures (T_c) have been chosen in the range between the melting temperature of the starting s-PS sample and its crystallization temperature measured by DSC scan in the cooling from the melt to room temperature. The starting material used in the isothermal crystallizations have been previously crystallized in the pure α or β form or in mixtures of α and β forms, for instance by cooling the melt

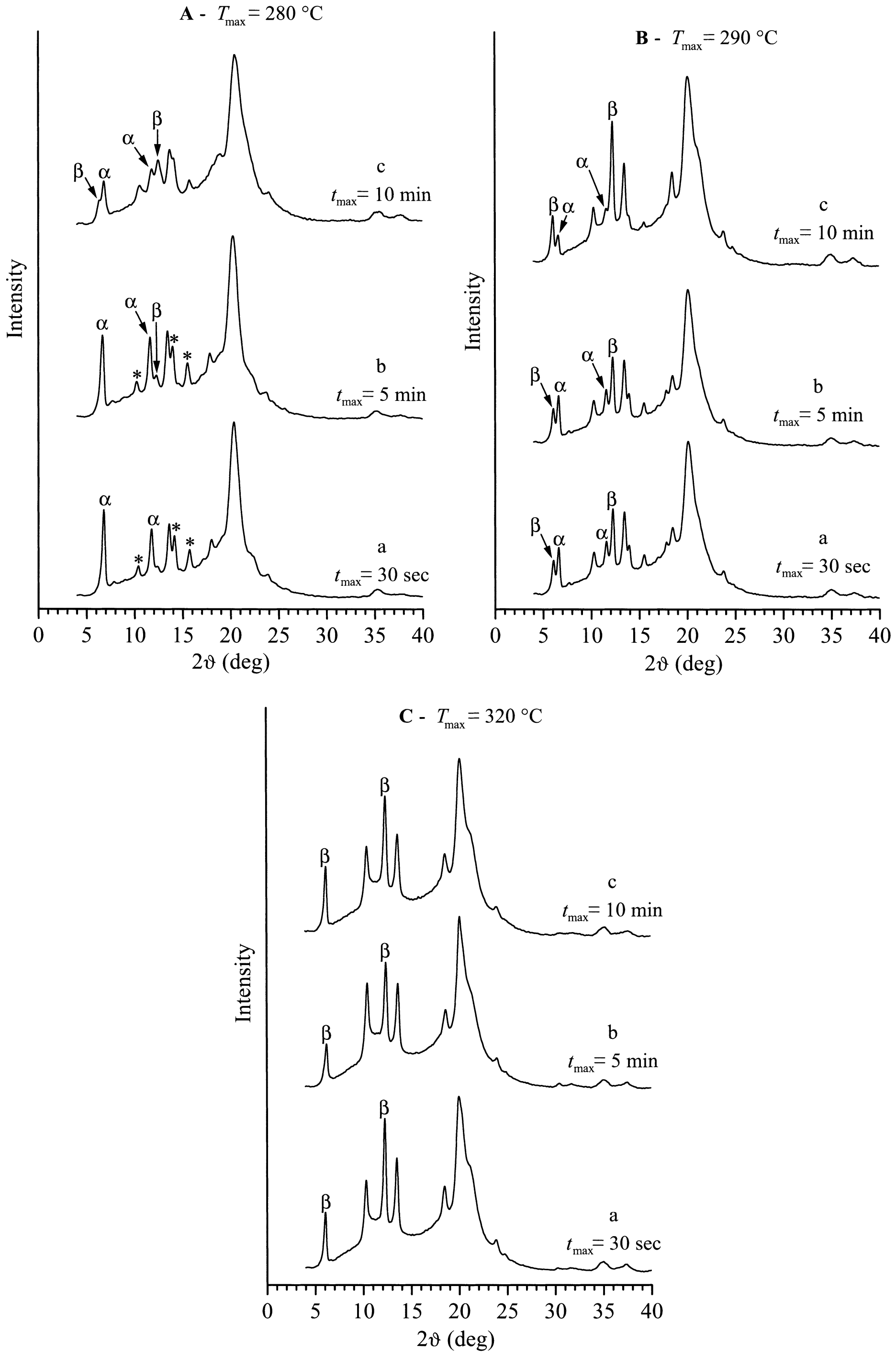

Fig. 2. X-ray powder diffraction profiles of s-PS samples crystallized from the melt by cooling to room temperature the melt heated at a given T_{max} temperature and kept at T_{max} for the indicated values of the time t_{max}. (A) $T_{max} = 280$ °C, (B) $T_{max} = 290$ °C and (C) $T_{max} = 320$ °C. The cooling rate is always ~10 °C/min. The reflections typical of the α and β forms are indicated. In (A) the asterisks in patterns a and b indicate the reflections typical of the limit ordered crystalline model α″.

from $T_{max} = 280, 320$ or 290 °C, respectively, as shown in the previous subsection (e.g. samples of Fig. 1a, e and b, respectively).

The X-ray diffraction profiles of samples isothermally crystallized from the melt at different crystallization temperatures T_c, starting from samples initially in the pure α form for $T_{max} = 280$ °C and $t_{max} = 30$ s, $T_{max} = 290$ °C and $t_{max} = 5$ min, and $T_{max} = 320$ °C and $t_{max} = 10$ min, are shown in Fig. 3(A)–(C), respectively. The presence of the reflections at $2\vartheta = 6.8°$ and 11.8°, typical of the α form and the absence of those at $2\vartheta = 6.2°$ and 12.3°, typical of the β form in all the X-ray diffraction profiles of Fig. 3(A) shows that for low values of T_{max} the samples always crystallize in the α form at

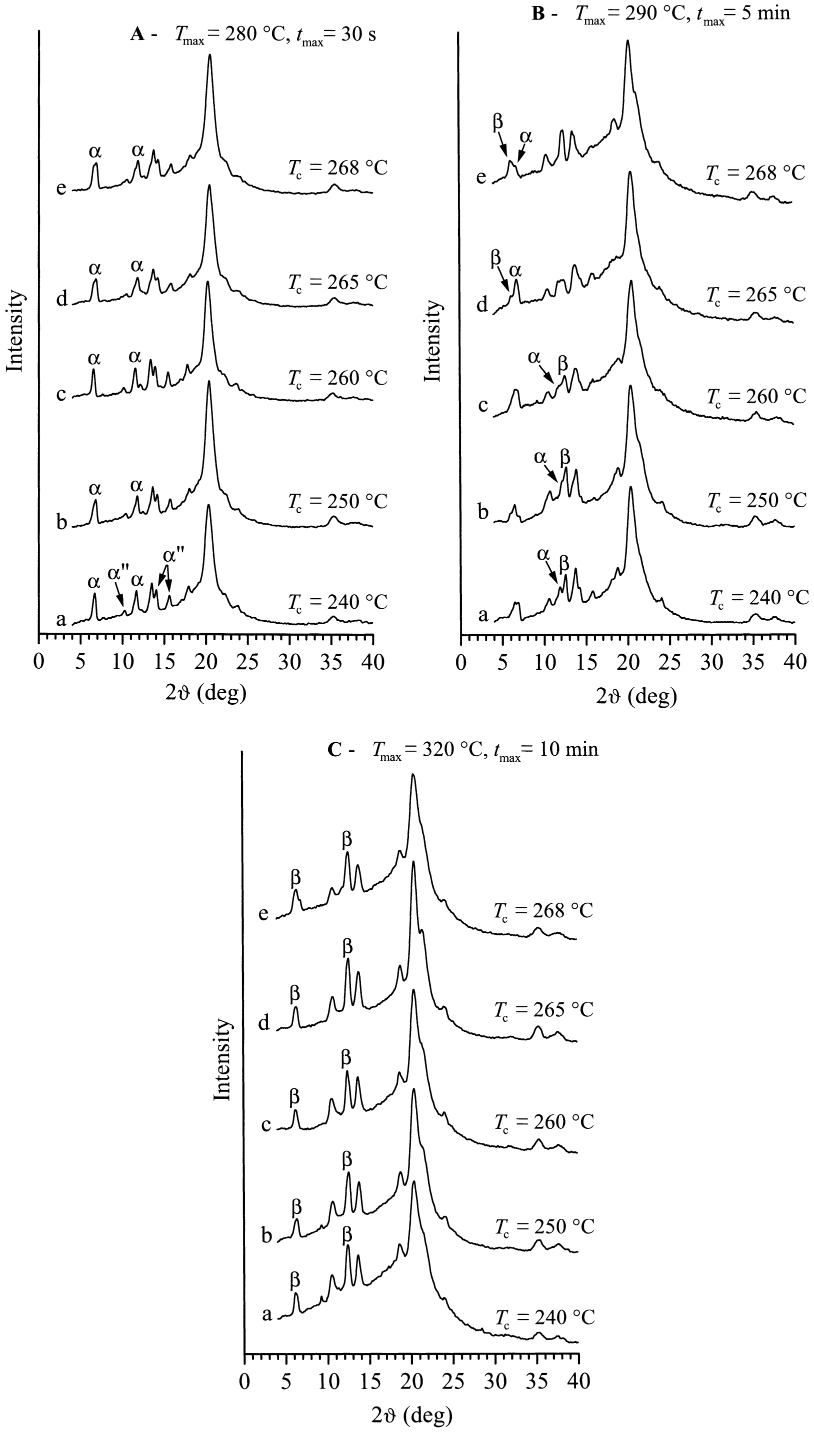

Fig. 3. X-ray powder diffraction profiles of s-PS samples initially in the α form isothermally crystallized from the melt at the indicated crystallization temperatures T_c for T_{max} = 280 °C and t_{max} = 30 s (A), T_{max} = 290 °C and t_{max} = 5 min (B) and T_{max} = 320 °C and t_{max} = 10 min (C). The reflections typical of the α and β forms are indicated.

any crystallization temperature. For higher T_{max} (e.g. T_{max} = 290 °C in Fig. 3(B)) samples in mixtures of α and β forms are obtained and the relative amount of the two forms in the crystalline phase seems to be quite independent of the crystallization temperature, at least in the range of accessible crystallization temperatures, between 240 and 268 °C. In fact, the ratio between the intensities of the reflection peaks at $2\vartheta = 11.8°$ and 12.3°, which gives a rough estimate of the content of α form in the crystalline fraction [4], is nearly constant with the crystallization temperature, for T_c higher than 240 °C. According to the results reported by Woo et al. [25] in these experimental conditions, at crystallization temperatures lower than 240 °C, the relative amount of α

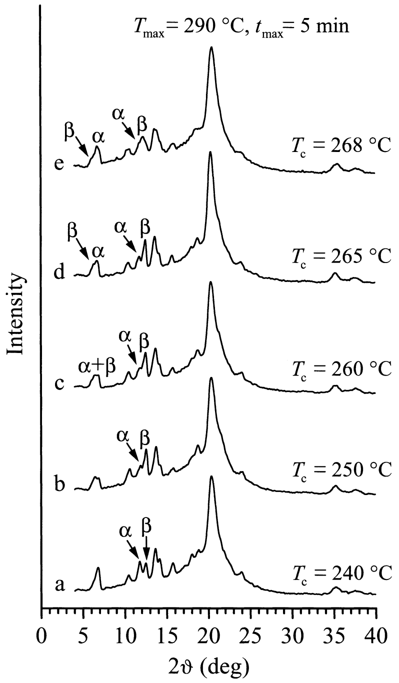

Fig. 5. X-ray powder diffraction profiles of s-PS samples initially in mixtures of crystals of α and β forms isothermally crystallized from the melt at the indicated crystallization temperatures T_c for $T_{max} = 290$ °C and $t_{max} = 5$ min. The reflections typical of the α and β forms are indicated.

and β forms depends on the crystallization temperature and, precisely, the lower the crystallization temperature, the greater the fraction of α crystals.

For the highest values of T_{max} and t_{max} (e.g $T_{max} = 320$ °C and $t_{max} = 10$ min in Fig. 3(C)), the samples always crystallize in the pure β form, at any crystallization temperature.

The X-ray diffraction profiles of samples isothermally crystallized from the melt at different T_c values, prepared from samples initially in pure β form for $T_{max} = 320$ °C and $t_{max} = 10$ min, $T_{max} = 290$ °C and $t_{max} = 5$ min, and $T_{max} = 280$ °C and $t_{max} = 30$ s, are shown in Fig. 4(A)–(C), respectively. In the latter case ($T_{max} = 280$ °C and $t_{max} = 30$ s) only the pattern of the sample crystallized at $T_c = 240$ °C is reported, as an example, since similar patterns are obtained at different T_c. It is apparent that when the starting material is in the β form, samples in the β form are always obtained upon melt crystallization, regardless of the crystallization temperature and of T_{max} and t_{max} values.

The X-ray diffraction profiles of s-PS samples obtained by isothermal melt crystallization at different T_c values, starting from samples initially in mixtures of α and β forms and for $T_{max} = 290$ °C and $t_{max} = 5$ min, are shown in

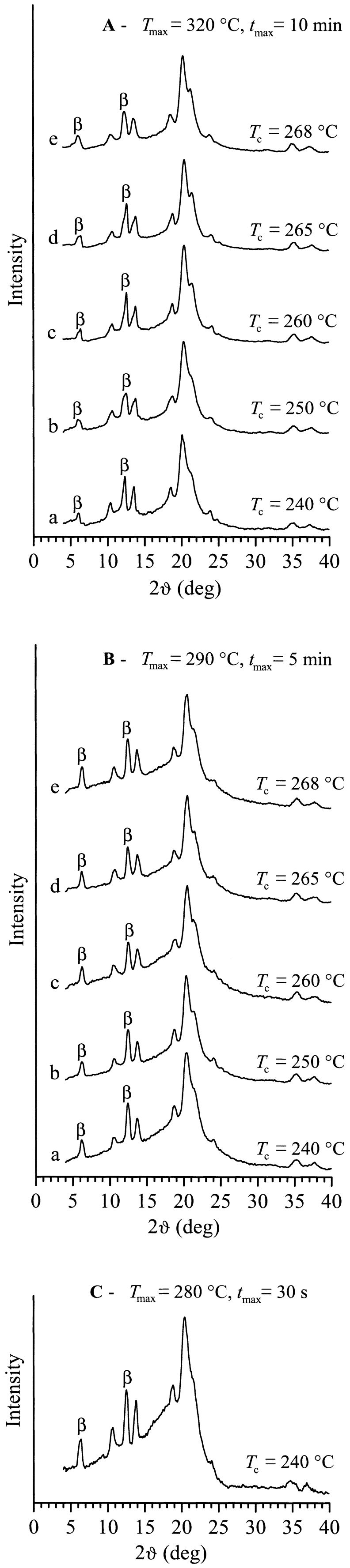

Fig. 4. X-ray powder diffraction profiles of s-PS samples initially in the β form isothermally crystallized from the melt at the indicated crystallization temperatures T_c for $T_{max} = 320$ °C and $t_{max} = 10$ min (A), $T_{max} = 290$ °C and $t_{max} = 5$ min (B) and $T_{max} = 280$ °C and $t_{max} = 30$ s (C). The reflections typical of the β form are indicated.

Fig. 5. Mixtures of α and β forms are obtained as indicated by the presence of the peaks typical of α ($2\vartheta = 6.8°$ and 11.8°) and β ($2\vartheta = 6.2°$ and 12.3°) forms. Therefore, if the starting material is a mixture of crystals of α and β forms, mixtures of both forms are obtained by isothermal melt crystallization, regardless of the crystallization temperature. As in Fig. 3(B), also in this case the relative amount of α and β forms depends on the crystallization temperature only at low temperature, in the range 240–250 °C, where the lower the crystallization temperature the higher the fraction of α form [25]. For higher T_{max} and t_{max} values, instead, the crystalline β form is always obtained, whatever the crystallization temperature.

These data indicate that when the melt is heated at temperature sufficiently high to erase the memory of the crystals of α form (e.g. $T_{max} = 320$ °C, Figs. 3(C) and 4(A)), the crystalline β form is always obtained by melt crystallization at any crystallization temperature, whatever the crystalline modification of the starting material. For lower T_{max} values, instead, the crystalline form obtained in melt-crystallized samples depends on the crystalline form of the starting material, but does not depend on the crystallization temperature. In particular, if the starting material is in the β form, the melt crystallized samples are again in the β form (Fig. 4(B) and (C)), whereas if the starting material is in the α form, samples in the pure α form are obtained for $T_{max} \leq 280$ °C (Fig. 3(A)), and mixtures of α and β forms for T_{max} in the range 280–300 °C (Fig. 3(B)).

On the basis on these results we can conclude that the crystallization of the pure crystalline α and β forms from the melt does not depend on the crystallization temperature, at least in the range of accessible isothermal crystallization temperatures, but mainly depends on the maximum temperature at which the melt is heated, the permanence time at that temperature and the crystalline form of the starting material. In other words the main factor controlling the formation of the α and β forms in melt crystallized s-PS samples is the memory of the α form in the melt. When this memory is preserved in the melt, e.g. for mild melting conditions and starting from material originally in the pure α form, the α form is obtained at any crystallization temperature. When there is no memory of α form in the melt, e.g. when the starting material is in the β form or when the melt is heated at high temperatures (at least 50 °C above the melting temperature of the starting material), the β form is always obtained at any crystallization temperature. According to the data reported in the literature [19, 21–25], our data indicate that the formation of α form is the result of a kinetically controlled process where the effect of the memory of the nuclei of α form plays an important role. When this effect is absent the thermodynamically more stable β form is always obtained in isothermal crystallizations at any accessible crystallization temperature in the range 240–270 °C.

The DSC scans of s-PS samples crystallized from the melt at various crystallization temperatures in the pure α (samples of Fig. 3(A), from $T_{max} = 280$ °C) and β (samples of Fig. 4(A), from $T_{max} = 320$ °C) forms are shown in Fig. 6(A) and (B), respectively. The DSC scans of samples crystallized at low temperatures exhibit multiple endothermic peaks. In particular, in the DSC scan of the sample crystallized at 240 °C in the α form (curve a of Fig. 6(A))

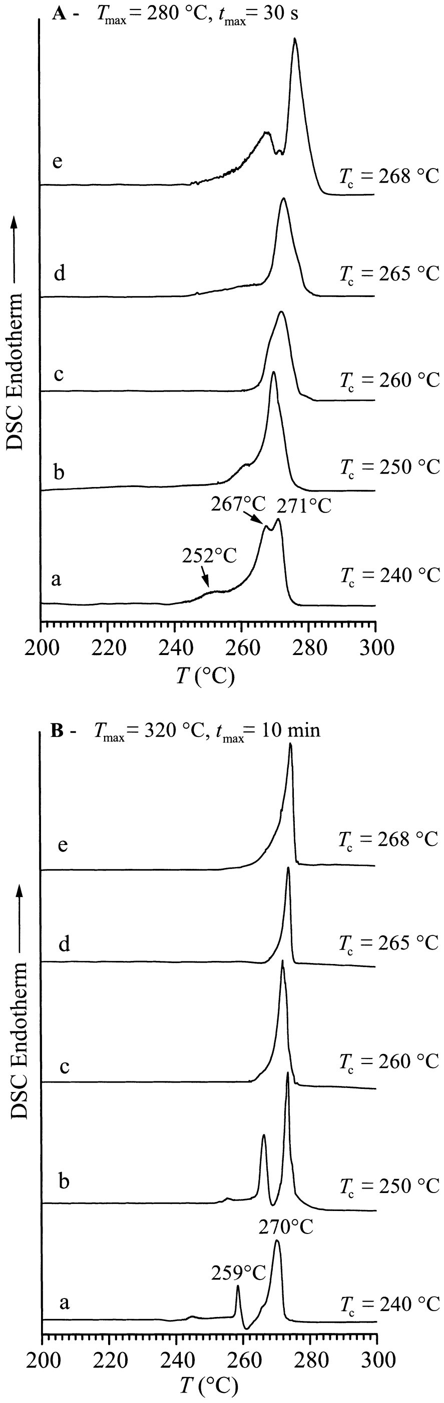

Fig. 6. DSC scans recorded at 2.5 °C/min of s-PS samples isothermally crystallized from the melt at the indicated temperatures T_c in the pure α form, for $T_{max} = 280$ °C and $t_{max} = 30$ s (A) and in the pure β form, for $T_{max} = 320$ °C and $t_{max} = 10$ min (B). The samples correspond to the samples of Figs. 3(A) and 4(A), respectively.

three peaks at 252, 267, and 271 °C are present, whereas in that of the sample crystallized at 240 °C in the β form (curve a of Fig. 6(B)) two peaks at 259 and 270 °C are present. In the case of β form, also the sample crystallized at 250 °C shows two melting peaks (curve b of Fig. 6(B)). The presence of multiple peaks in the DSC scans of crystals of α and β forms has already been discussed in the literature [21,23,25]. The occurrence of reorganization involving only a lamellar thickening process, in the case of the β form, and a reorganization involving either lamellar thickening or transformation of α into β form, in the case of the α form, have been suggested [25]. In particular, in the case of melting of the α crystals, showing three peaks, the authors have speculated that the lowest melting peak would correspond to the melting of individual α form, whereas the intermediate peak at 267 °C involves a lamellar thickening process and a transformation of α to β form possibly combined with reorganization of the β form [25].

The presence of recrystallization during the melting of both α and β forms crystallized at low temperatures is clearly indicated by the change in the relative areas of the two endothermic peaks with the heating rate, as shown in the DSC scans of Fig. 7(A) and (B) for the α and β forms, crystallized at 240 °C, respectively, and in Fig. 7(C) for the β form crystallized at 250 °C. It is apparent that for both α and β crystals, the area of the peak at high temperature increases and that of the peak at low temperature decreases, with decreasing heating rate. The peak at high temperature disappears at high heating rate in the case of the sample crystallized in β form at 250 °C (curve c of Fig. 7(C)). According to the results discussed by Woo et al. [19] the recrystallization processes are absent or very slow for α and β forms crystallized at high temperatures and are faster for the β crystals than for the α ones, as also indicated by the presence of an exothermic effect after the first melting peak in the DSC scan of the β form sample crystallized at 240 °C (curves a of Figs. 6(B) and 7(B)).

In order to analyze the suggested possibility that the recrystallization process involves a transformation of α into β form [25], X-ray diffraction measurements of the sample crystallized at 240 °C in the α form, were performed at different temperatures within the temperature range between the lowest and highest melting peaks observed in the corresponding DSC scan (curve a of Fig. 6(A)). The X-ray diffraction patterns recorded at different temperatures are shown in Fig. 8. All the X-ray diffraction profiles of Fig. 8 are characterized by the presence of the reflections at $2\vartheta = 6.8°$ and 11.8°, typical of the α form, and by the absence of those at $2\vartheta = 6.2°$ and 12.3°, typical of the β form. This indicates that no structural transition from the α

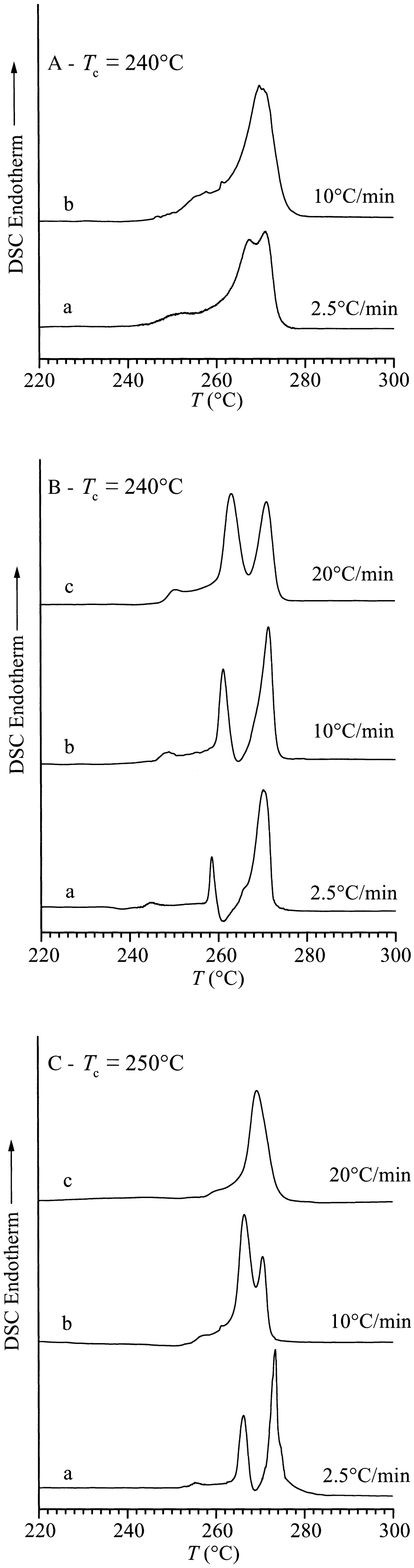

Fig. 7. DSC scans recorded at the indicated heating rates of s-PS samples isothermally crystallized form the melt at $T_c = 240$ °C in the pure α form (A), at $T_c = 240$ °C in the pure β form (B) and at $T_c = 250$ °C in the pure β form (C).

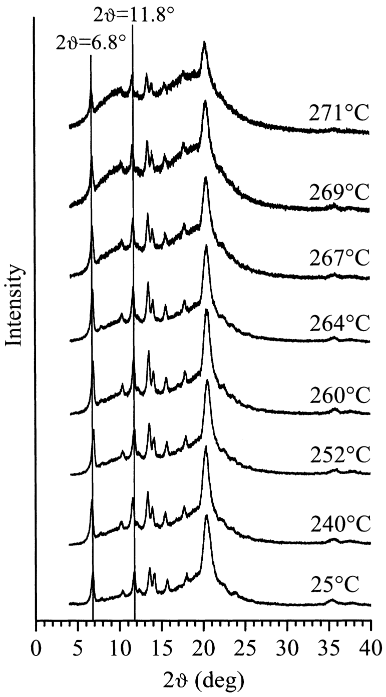

Fig. 8. X-ray powder diffraction profiles recorded at the indicated temperatures during the heating of a s-PS sample in the α form isothermally crystallized from the melt at 240 °C for $T_{max} = 280$ °C and $t_{max} = 30$ s (sample of curve a of Fig. 3(A)).

to the β form occurs during the heating of the α crystals. Therefore, the recrystallization process shown in the DSC scans of Figs. 6(A) and 7(A) only involves lamellar thickening of the α crystals.

4. Conclusions

The crystallization of α and β forms of s-PS from the melt is strongly affected by a variety of experimental parameters, as the maximum temperature of the melt (T_{max}), the permanence time of the melt at that temperature (t_{max}), the crystallization temperature (T_c), the cooling rate and also the crystalline form of the starting material.

The structural analysis of s-PS samples crystallized from the melt in non-isothermal and isothermal conditions has indicated that the polymorphic behavior of s-PS does not depend on the crystallization temperature, at least in the range of accessible isothermal crystallization temperatures, between 240 and 270 °C. The crystallization of the α and β forms is mainly dependent on the maximum temperature of the melt (T_{max}). In particular, for high T_{max} values, at least 50 °C above the melting point of the starting material, the sample crystallizes always in the β form, regardless of the crystallization temperature and the crystalline form of the starting material. For lower T_{max} values, the formed crystalline modification does not depend on the crystallization temperature, in the range of accessible temperatures, but depends on the crystalline form of the starting material. If the starting material is in the β form, the melt crystallized samples are again in the β form, whereas if the starting material is in the α form, samples in the pure α form are obtained for low values of T_{max} (10 °C above the melting point of the starting material and kept for short time at that temperature, e.g. $T_{max} = 280$ °C, $t_{max} = 30$ s). For higher values of T_{max}, in the range 280–300 °C, mixtures of crystals in the α and β forms are obtained. In other words a pure α form is obtained only when a memory of the α form crystals is still present in the melt, when this memory is erased the thermodynamically more stable β form is always obtained.

Relevant recrystallization phenomena occur during the melting of the sample crystallized from the melt at low crystallization temperatures and involve only lamellar thickening of the same crystalline modifications (α or β), but no structural transitions. These recrystallization processes are responsible of the multiple melting peaks observed in the DSC scans of the pure α and β forms of s-PS.

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