行政院國家科學委員會補助專題研究計劃成果報告

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※ 半結晶性高分子系之多晶相形態、熱行為 ※
※ 及排向性質之比較(1/3, 2/3, 3/3) ※
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目錄

目錄 ................................................................. 1
英文摘要 ............................................................. 1
中文摘要 ............................................................. 2
成果發表 ............................................................. 3
研討會報告 ........................................................ 5
結果與討論 ....................................................... 6
結論 ................................................................. 9
參考文獻 ........................................................... 10
附錄 ................................................................. 17
Abstract

Crystal polymorphism, conformations, and transformation of syndiotactic polystyrene (sPS) thin film cast from solvents were investigated via wide angle X-ray diffraction (WAXD), transmission electron microscopy (TEM), electron diffraction (ED), differential scanning calorimetry (DSC), and Fourier-transform infrared spectroscopy (FT-IR). This solvent is unique in the 1,1,2,2-tetrachloroethane solvent induced sPS to develop a γ-crystal. The solvent-induced γ-crystal exhibited a crystalline morphology having small crystal aggregates with an average size less than 100 nm. Upon heating, the γ-crystal gradually grew into much perfect packing, and finally went through a γ → α' transformation at temperature of 200°C. Thermal transitions of the initial solvent-induced crystalline γ-form in neat sPS exhibited some similarity. Initial solvent-induced crystalline γ-form in sPS/aPS blends or those in neat sPS samples were heated to temperatures above 200°C. A re-organization of the melted crystalline γ-form originally present in the solvent-cast in neat sPS both led to formation of crystalline α'-form. On the other hand, crystal/conformation transformations can be thermal-induced in syndiotactic polystyrene films treated with different solvents. The thermal-induced phase transition from the δ to ordered γ then to α' phase was successfully proven for the sPS/o-dichlorobenzene complex. Similarly, the other sPS/1,2-dichloroethane complex underwent transition (from δ to disordered γ then to α' phase) upon the same thermal treatments.

The achievement of this project contains part of results presented briefly in this report. Other in-depth results are listed as academic publication, followed by the conference presentations listed below. In addition, a review paper is presented at last to make the report complete.
中文摘要

本計劃探討以X 光繞射儀(WAXD)、透射式電子顯微鏡(TEM)、
電子繞射(ED)、微分掃瞄熱度計(DSC) 和傅立葉轉換紅外線光
譜儀(FTIR) 研究以溶剤成膜的間規排向聚苯乙烯(sPS)，探討其
多晶態、結晶型態及轉換。1,1,2,2-四氯乙烯是唯一可以誘導 sPS 形成
γ晶態的溶剤，溶剤誘導的γ結晶的型態，是由平均小於 100nm 的結晶
聚集所形成。經由加熱，在 200℃ 時，γ晶態會逐漸變為較完美的堆
積，而最後會有γ→α'的轉變，sPS 的溶剤誘導γ結晶，對熱轉變有些
許的相似性，純的 sPS 加熱至 200℃ 以上時，熔融的γ結晶會再結晶
形成α'晶態。另一方面，不同溶剤處理的 sPS 膜可以由熱誘導其結晶
型態的轉換，對於 sPS 和鄰-二氯苯(o-dichlorobenzene)的複合系統，
δ晶態可由熱誘導轉變為較有規則性的γ晶態，然後再轉變為α'晶態。同
理，sPS 和 1,2-二氯乙烷(1,2-dichloroethane) 複合系統在相同的熱
處理下，δ晶態可由熱誘導轉變為較不規則的γ晶態，然後再轉變為α'
晶態。

本計劃成果包含本報告內代表性結果所示(簡述)，其餘詳盡結果
如下學術發表所列，會議報告亦陳列如後，另外有一篇 review paper
的發表，附列於後綜合本計畫之成果。
本計畫成果可包含下列發表


研討會報告


結果與討論

有越來越多的研究說明FT-IR可以解釋溫度誘導多晶態的改變，經由不同溫度恆溫熱處理的sPS以FT-IR來定性，Fig. 1(A)和(B)表示頻率範圍在440-640cm⁻¹之間，以1°C/min的升溫速度，在不同溫度下所得到之光譜。Fig 1(A)中IR的結果可以證明結構的改變，在502、510和572cm⁻¹的位置是由於TTGG序列所造成，在200°C下可以發現有些微的減小，最後當完全由helix轉變為trans時，這些位置的峰會消失，而539cm⁻¹位置的吸收強度隨著這樣的相轉變增加。在195-205°C之間，539cm⁻¹位置吸收強度增加是因為TTTT/GTTG構形有關，亦即all-trans的局部構形產生結構的改變。

Fig. 2說明溶液成膜的sPS在相似的熱處理之下，頻率在820-1000cm⁻¹之間的FT-IR圖譜，很顯然的，841和906cm⁻¹表示sPS有helical構形，在60-195.6°C之間沒有顯著的變化，但在200.5°C以上，852和902cm⁻¹的吸收峰開始浮現，隨著熱處理溫度的增加，841和906cm⁻¹吸收峰的強度逐漸減小，這說明helical chains轉變為zigzag結構。此外值得注意的是由helical chains堆積結構造成的932和945cm⁻¹的吸收峰，在60-200°C之間的位置和強度沒有變化。進一步說明溶液成膜的sPS在緩慢熱處理下熱誘導晶相改變，利用XRD證
明晶態結構，Fig. 3 說明在溶劑不存在下 80-200°C 之間每隔 20°C 的 XRD 圖，繞射峰位置在 2θ=9.2、15.6、17.2、19.9、21.1 和 28.3° 是γ 態結晶所造成，亦指出在最初成膜的 sPS 就直接產生γ態。

另外一方面，XRD 也用來檢視溶劑處理過但尚未熱處理的 sPS 樣本，Fig. 4 的 XRD 光譜分別表示含有少量鄰-二氯苯和 1,2-二氯乙烷的 sPS 繞射行為。最早由 De Rosa 等所提出 1,2，δ晶態所造成繞射峰的位置 2θ=7.8、9.9、16.8、18.5、23.1、24.5 和 28.1°。圖中 a 曲線為鄰-二氯苯誘導δ晶態，所得到的繞射位置與文獻非常類似(2θ=7.9、9.7、13.4、17.4、20.4、23.2、24.5 和 28.3°)，相同的結果也發生在 1,2-二氯乙烷所誘導的結晶。這兩種繞射行為證明了兩種不同的δ結晶，分別為鄰-二氯苯和 1,2-二氧乙烷殘存下的 sPS 鏈堆疊。將兩種不同溶劑所誘導的 sPS 樣品乾燥以去除溶劑，可以得到溶劑誘導的δ晶態，所得到兩種δ晶態再以 DSC 測其熱行為，Fig. 5 顯示不同溶劑誘導的 sPS 樣品。(a)曲線為鄰-二氯苯所誘導的系統(b)為 1,2-二氯乙烷所誘導系統。(a)曲線顯示在 155°C 時有一熔融峰，這一個熔融峰是δ晶態轉變為γ晶態所造成，另外在 209°C 有一個小熔融峰，一般認為這是因為γ晶態再結晶成α’晶態 1，而 271°C 的吸熱峰是α’晶態熔融的結果。就如同 sPS/1,1,2,2-四氧乙烷或其他溶劑誘導 sPS 結晶 1,3-6，γ→α’晶態轉變通常會在 DSC 掃描過程中發生，且會在 200°C 產生明顯的
吸熱峰，最後均會在 271°C 融掉α'晶態。然而由 1,2-二氯乙烷所誘導δ晶態，只因結構改變，在 150-176°C 產生很寬的熔融峰。

進一步利用 XRD 探討溶劑誘導結晶隨著加熱處理所造成的相轉變。Fig. 6 表示溶劑所誘導的結晶在 60-240°C 的範圍之間，每隔 20°C 所得到的繞射光譜。在 Fig. 6(A)中，γ晶態存在於 140°C 以上，而當溫度大於 200°C 時，α態變成 sPS 的主要晶態，至於 sPS/1,2-二氯乙烷複合體中的δ晶態，在 140°C 時會有δ態轉變為γ態的現象產生，然後γ態進一步轉換成α'晶態。Fig 6(B)顯示在 160-200°C 之間，γ態會轉換成α'晶態。
結論

以往的文獻中，γ晶態皆是由δ態結晶在高溫下熱處理轉變而來，但本研究中，γ晶態可以直接由1,1,2,2-四氯乙烷誘導SPS結晶，不需要熱處理得到，在這系統中沒有δ態轉變為γ態的現象。當溶劑所誘導的結晶在更高的溫度下熱處理，會進行結晶相的轉變，而形成較穩定的結晶態(α'或β)。同時也發現當緩慢加熱，γ→α'會在快速再結晶時發生。

另一方面，SPS/1,2-二氯乙烷複合體會形成δ結晶，接近第一次轉變溫度時會變成不規則γ態，在更高溫度(160°C)下會由不規則γ態轉變為α'態。較規則γ態結晶可由SPS/鄰-二氯苯複合體的δ結晶在去除溶劑後得到，繼續提高熱處理溫度至195°C時，γ態會快速熔融再結晶成α'態。
参考文献


Fig. 1 FTIR spectra of solution-cast sPS sample having been subjected to step-wise increase of 10°C in the range 60-245°C.
Fig. 2  FTIR spectra in the frequency ranging from 820 to 1000 cm\(^{-1}\) for the sPS sample subjected to step-wise increase of 5°C in the temperature range 60-245°C.
Fig. 3 XRD patterns of a solution-cast sPS film further subjected to step-wise temperature increase of 20°C from 60-240°C.
Fig. 4 XRD powder patterns of δ-type crystal in (A) sPS/o-dichlorobenzene complex, and (B) sPS/1,2-dichloroethane complex.
Fig. 5 DSC traces (at 20°C/min) of δ-type crystal in (A) sPS/o-dichlorobenzene complex, and (B) sPS/1,2-dichloroethane complex.
Fig. 6 XRD patterns showing transition of initial δ-type crystal in (A) sPS/o-dichlorobenzene complex, and (B) sPS/1,2-dichloroethane complex, respectively, subjected to 20°C step-increase of temperature in the range 60-240°C.
Polymorphism, thermal behavior, and crystal stability in syndiotactic polystyrene vs. its miscible blends

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Abstract

Four crystal types (α, β, γ, δ) and some mesophases/sub-modifications have been identified and discussed in syndiotactic polystyrene (sPS). The α- and β-forms are the main crystal packing forms in thermally-processed sPS, while the γ- and δ-crystals are identified only in solvent-treated sPS. In addition, the δ- and γ-forms are of a monoclinic crystal cell (with helical chain conformation) and the cell dimensions depend on the types and amount of residual solvent trapped in the crystal. The δ- and γ-crystal in solvent-treated sPS are more like mesophases that transform readily to the α-, β''- or β'-crystal upon heating the solvent-treated sPS to high temperatures near melting. This review thus focuses on studies of the α, β-crystals in sPS, and provides comprehensive discussions on the thermal behavior, crystal structures, thermodynamics, kinetics, and stability of these two major crystal packings (α vs. β) in sPS upon melt crystallization in comparison with cold crystallization. Analyses of melting behavior, diffractograms, or IR spectra, etc. of SPS can be complicated by the presence of co-existing polymorphic crystals. In general, a total of four melting peaks (labeled as P-I, P-II, P-III, P-IV from low to high temperatures) have been identified in a melt-crystallized sPS that typically contains mixed fractions of both crystals. By refining the techniques of obtaining sPS with individually isolated α- or β-crystal, recent studies have been able to correct suspected inaccuracy of some thermodynamic and kinetic measurements in earlier studies and to interpret the relative stability of the various crystals in SPS. SPS samples could be prepared such that they contained purely isolated α- or β-crystal, and the individual crystal types are used for more precise characterization of analysis. The P-I and P-III melting peaks are attributed to the β'-crystal while the P-II and P-IV peaks are attributed to the α''-type. In addition, kinetic and thermodynamic characterization has been thoroughly performed on individually isolated crystal types. The α-crystal of sPS has a lower melting temperature than the β-crystal, with \( T_{m,α} = 281.7°C \) and \( T_{m,β} = 288.7°C \). The crystallization kinetics of the α-crystal is a heterogeneous nucleation with higher rates while the β-crystal is a homogeneous nucleation with lower rates. The β'-type is more thermodynamically stable than the α''-type; but the α''-type is kinetically more favorable. In addition, although there is literature report concerning a transformation of δ or γ mesophase crystals to α- or β-crystal, there is no evidence showing a solid-solid transition from the α- to β-crystal or β- to α-crystal during normal thermal processes. It

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suggestions that both α- to β-crystal are stable solid and transformation between them can only be achieved by melting and re-packing. This could be fully explained using a stability/metastability chart of free energy vs. temperature. Nevertheless, the individual melting/reorganization of these two crystals might undergo crystal transformation via solid–liquid–solid transition. The crystallization kinetics of β'-crystal is a homogeneous nucleation with lower rates. By comparison, crystallization kinetics of the α-crystal is a heterogeneous nucleation with higher rates. Microscopy characterization also revealed a highly nucleated crystallization of the α-crystal. The effect of blend miscibility on the polymorphism behavior in sPS is also discussed. The effects of miscibility on polymorphism was investigated by studying miscible blends of sPS with atactic polystyrene (aPS) or sPS with poly(1,4-dimethyl phenylene oxide) (PPO). Miscible blends containing sPS have been found to favor growth of β'-crystal than neat sPS when subjected to the same melt crystallization conditions. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Syndiotactic polystyrene; Polymorphism; Crystal; Phase stability; Thermal behavior; Multiple melting; Cold crystallization; Melt crystallization; Kinetics; Thermodynamics

Abbreviations: sPS: syndiotactic polystyrene; iPS: isotactic polystyrene; aPS: atactic polystyrene; DSC: differential scanning calorimetry; SEM: scanning electron microscopy; WAXD: wide-angle X-ray diffraction; POM: polarized-light optical microscopy; FT-IR: Fourier transform infrared spectroscopy; $T_m$: temperature of cold crystallization; $T_c$: temperature of melting peak; $T_g$: glass transition temperature; $T_m^{max}$: maximum melting temperature at molten state prior to melt crystallization; $M_w$: weight average molecular weight; $\Delta H_{fcr}$: heat of fusion for the α-crystal; $\Delta H_{fb}$: heat of fusion for the β-crystal

Contents

1. Introduction .......................................................... 946
2. Crystal forms in thermally-processed sPS ......................... 947
   2.1. α-Crystal ................................................... 948
   2.2. β-Form crystal ............................................. 950
3. Crystal morphology and thermal behavior of thermally-processed sPS ................................................. 951
   3.1. Crystal melting behavior .................................... 951
   3.2. Equilibrium melting temperature of α- and β-crystals .... 954
   3.3. Effect of maximum temperature on crystal forms ........ 956
   3.4. Crystallization kinetic analysis of α- vs. β-forms ...... 960
   3.5. Effect of miscibility on polymorphism ................. 963
   3.6. Relative stability of α- vs β-crystals in neat sPS .... 964
   3.7. Relationships between polymorphic crystals and multiple melting .............................................. 966
   3.8. Identification of crystal forms and spherulites in cold-crystallized sPS ........................................ 968
   3.9. Effects of tacticity and molecular weight ............... 975
4. Crystal forms in solvent-treated sPS ................................ 977
5. Conclusion .................................................................. 979
Acknowledgements ....................................................... 980
References ................................................................. 981

1. Introduction

Since its successful commercial synthesis using stereo-specific polymerization in as early as 1985 [1–3], syndiotactic polystyrene (sPS) has been widely studied. Most semicrystalline polymers possess only one type of unit crystal cell; for others, polymorphisms are known to exist. It is known that sPS exhibits complex polymorphism [4–8] and multiple melting endotherms [9–14]. Generally speaking,
there exist four crystal forms (α, β, γ, and δ) in thermal- or solvent-treated sPS [15–19]. A combination of \( \alpha'' \) and \( \beta' \)-crystals is produced when melt-crystallized at low temperatures and the fraction of \( \beta' \)-type crystal increases with successive increase in isothermal temperatures [9,10]. Only \( \beta(\beta') \)-type crystal is generated in sPS if melt-crystallized at temperatures above 260°C with no \( \alpha \)-crystal (neither \( \alpha' \) nor \( \alpha'' \)). The relative fraction of \( \alpha'' \)- and \( \beta' \)-type crystals can be influenced as a function of isothermal melt crystallization temperatures. In addition, the maximum melting temperatures erasing thermal history and residence time in the melt also have a significant effect on the polymorphism of sPS [14]. Furthermore, polymorphism state of sPS can be altered in the presence of other miscible polymers, e.g. poly(2,6-dimethyl-p-phenylene oxide) (PPO) or atactic polystyrene (aPS) [20–22]. Both the \( \alpha'' \) and \( \beta' \)-type crystals are observed in the neat melt-crystallized sPS; however, only the \( \beta' \)-crystal is found in miscible sPS/aPS or sPS/PPO when crystallized at the same conditions. Apparently, blending with the miscible amorphous polymer reduces the possibilities of the formation of \( \alpha \)-type crystal in sPS. In addition, cold crystallization (in contrast with melt crystallization) has a dramatically different effect on the polymorphism of sPS [23–26]. Only the \( \alpha' \)-type crystal (containing two modifications — \( \alpha'' \) and \( \alpha'' \)), and not the \( \beta' \)-type one, is generated if sPS cold-crystallized from its amorphous glassy state.

Many studies investigated phase transformation in sPS by using Fourier transformation infrared (FT-IR) and/or Raman spectroscopy, differential scanning calorimetry (DSC), and X-ray analysis, etc. [27–36]. Correlations between the polymorphism and multiple melting endotherms have been an interesting subject of study. Co-existing \( \alpha'' \) and \( \beta' \)-type crystals (or other additional crystal forms) inevitably lead to multiple melting endotherms. Moreover, presence of polymorphic crystals in sPS can further complicate the melting and thermal behavior. Interpretation of phase transition (transformation between different crystals) may be additionally complicated by phenomena of multiple melting behavior in sPS. Two possible mechanisms are common. One is dual morphology or polymorphism, suggesting that pre-existing multiple crystals or scanning-induced crystal alterations are responsible. The other mechanism is re-organization, which states that the polymer containing an originally less perfect crystal form, but the pre-existing lamella or crystal of lower degree of perfection may transform to a more perfect lamellae or crystal during heating scans. Four melting endothermic peaks (labeled as P-I, P-II, P-III and P-IV in the increasing order of temperature location) are seen in isothermal-treated sPS [13]. However, many other polymers containing only a single crystal can also exhibit melting (dual or triple melting peaks). For example, sPS containing only the \( \alpha'' \)-type exhibits dual melting peaks upon DSC scanning [26]. It is of interest to know which crystal of sPS is associated with the observed melting peaks. In addition, it is critical to understand what major differences there are between these two crystal types in thermal, morphology, kinetics, etc., of sPS. Miscibility affects both kinetic and thermodynamic states of sPS when blended with other polymers. Effects of miscibility are expected on the polymorphism and thermal behavior of sPS. To our knowledge, a comprehensive review on polymorphism and thermal transition behavior of sPS and its miscible blends has not appeared in the literature. In the past decade, only a review article on synthesis and catalysis of sPS appeared in 1996 [37]. This review article on morphology, melting, crystals, and miscible blends of sPS was written to serve a timely need on this important subject. Most references cited and discussed here are those that appeared in the recent past 10 years between 1991 and 2000.

2. Crystal forms in thermally-processed sPS

Four different unit cell forms (α, β, γ, δ) can be obtained in sPS depending on the thermal
histories and/or solution treatments that have been explored in many related studies [38–42]. The unit cells of these four forms are distinctly different. Normally, co-existing α- and β-forms are obtained in various relative fractions in melt-processed sPS. The α- and β-forms are more common and associated with polymer chains in trans-planar (zig-zag) conformation while the γ- and δ-forms are of a helical conformation that are commonly associated with solvent-induced crystallization in sPS [19]. Only two crystal forms, α- and β-crystals, are commonly found in sPS subjected to various thermal treatments. These two crystalline forms (α and β) are of a planar zig-zag conformation in their backbone chains [4–8]. Each of the α-form (a hexagonal unit cell) and β-form (an orthorhombic unit cell) can be sub-classified as two different modifications characterized by differing degrees of structural order, which are described as α' and β' and the others are two limited-order modifications (α'' and β'') [15–19]. Two less common crystalline forms are δ and γ, which are characterized by their main chain in s(2/1)2 helical conformation [4–8]. Interestingly, it was shown that solvent-induced δ-type, by casting at 60°C from solution, can transform to γ-type, and then again to α'-type crystal during slow heating at a scan rate of 20°C/min [6]. Another transition is that the δ-type crystal transforms to β'-crystal directly during annealing at a presetting temperature of 160°C. Under high pressure compressed CO₂, solid–solid transformation of α'-type to β'-type has been reported [36]. But transition between α''- and β''-type is yet to be proven or refuted [12–14]. Relative stability of different crystal type apparently varies. This review will also discuss this subject.

First, the unit cells of α- and β-forms in sPS are discussed here. The γ- and δ-forms are not usually seen in melt-processed sPS and commonly associated with solvent-induced crystallization in sPS [19]. The less common γ- and δ-forms in solvent-treated sPS will be discussed in later sections.

2.1. α-Crystal

Two proposed packing models for the α-form crystal of sPS [5,15,18] are shown here.

(A) Hexagonal model proposed by Greis et al., space group P62c (a = b = 26.25 Å, c = 5.04 Å)
(B) A trigonal model proposed by De Rosa et al., space group \(P3_1\). \((a = b = 26.26 \, \text{Å}, c = 5.04 \, \text{Å})^1\)

In addition, it is generally accepted that there are two sub-modifications for the \(\alpha\)-crystal: a limit-ordered \(\alpha''\)-modification and a limit-ordered \(\alpha'\)-modification. Models for the \(\alpha''\)-Modification (schematics A and B) and \(\alpha'\)-modification (schematic C) \([5,15,18]\).

\[\text{Diagram of \(P3_1\) structure with \(\alpha''\) and \(\alpha'\) modifications.}\]

\(^1\) Relative heights of the centers of phenyl rings are in units \(c/6\). Dotted lines in B indicate crystallographic glide planes \(c\). In A, glide planes \(c\) contain the axes of the unit cell.
2.2. β-Form crystal

The β-form is an orthorhombic unit cell and the chain conformation is all-trans planar zig-zag. It is generally accepted that there are two sub-modifications for the β-crystal: a limit-ordered β'-modification and limit-ordered β"-modification. The β'- and β"-forms are both orthorhombic, with a unit cell dimensions: \( a = 8.81 \, \text{Å}, b = 28.82 \, \text{Å}, c = 5.51 \, \text{Å} \).

Model of packing proposed for the limit-ordered β'-modification [16,19]:

Model proposed for the limit-ordered β'′-modification is as follows [16–19]:

The approximate \( z \) fractional coordinates of the barycenters of the phenyl rings are also shown.

\(^2\) The carbon atoms of the asymmetric unit are labeled with the numbers 1–16.
3. Crystal morphology and thermal behavior of thermally-processed sPS

3.1. Crystal melting behavior

Upon melt crystallization of sPS at most accessible temperatures (230–260°C), it has been proven that sPS develops two major crystals (α and β) with four sharp discernible melting peaks (P-I, P-II, P-III, P-IV) associated with these two different crystal lamellae [13]. In general, the α-crystal packing can become an alternative route in sPS crystallization under three conditions: (1) slow cooling from molten state, (2) melt crystallization at low temperatures (e.g., 230°C or lower), or (3) cold crystallization from quenched glass. As a matter of fact, cold-crystallized sPS samples contain only α-type crystal [10], which differs significantly from melt-crystallized sPS in crystal forms or the shapes of melting endotherms. By comparison, melt crystallization of sPS at most accessible temperatures produce both α-type (P-II, and P-IV) and β-type (P-I and P-III) crystals of various fractions. In general, the low to medium melt crystallization temperature always result in growth of β-crystal and α-type, but higher melt crystallization temperature tends to favor greater fractions of β-type. As a matter of fact, the β-type crystal became the only dominating species if sPS was melt-crystallized at temperatures equal to or higher than 260°C. Under conditions approaching "equilibrium", only the β-crystal is present and is the favored type of packing.

By refining the techniques of obtaining sPS with individually isolated α- or β-crystal [6,13,26], recent studies have been able to correct suspected inaccuracy of some thermodynamic and kinetic measurements in earlier studies. sPS samples could be prepared so that they contained purely isolated α- or β-crystal, and the individual crystal type is used for more precise characterization for analysis. Some of the results are discussed here. For example, sPS samples could be prepared in such a way that they contained only the α-crystal and no β-crystal or others. One of the technique is briefly discussed as follows. The initial starting form of sPS was a quenched amorphous glassy material, then the sPS material was treated at a maximum temperature ($T_{\text{max}}$) of 280°C for 1 min before being subjected to melt crystallization at a series of temperatures. Such thermal treatments led to only α″-crystal with no β′-form in sPS. Fig. 1 reveals the X-ray diffraction spectra of the neat sPS sample containing only α″-type without β′-type production after being melt-crystallized at different isothermal temperatures: 230, 240, 250, and 260°C. The X-ray results showed the diffraction peaks corresponding to only the α″-type. Note that earlier studies have shown that if $T_{\text{max}}$ is higher than 280°C, then not only α- but also β-form can be simultaneously produced upon the same melt crystallization. Thermal history might not have been erased completely during melting at 280°C for 1 min. Thus, the initial form of starting material may play a significant role on the polymorphism. It is discussed in detail in Section 3.2.

Next, a different set of sPS samples were prepared, which contained only the β-form crystal. Solution-cast sPS (containing β″-type crystal) was first heated at $T_{\text{max}} = 380°C$ for 0.5 min in the DSC and then quenched to one of the pre-setting isothermal temperatures (230, 240, 250, and 260°C) for 240 min. The crystals in the melt-crystallized sPS samples were then characterized. Fig. 2 is the X-ray diffraction spectra showing only β′-type in sPS melt-crystallized at the temperatures of 230, 240, 250, and 260°C. For all temperatures (230–260°C), only the β′-type was found in the melt-crystallized sPS ($T_{\text{max}} = 380°C$, 0.5 min). The initial forms as well as $T_{\text{max}}$ at melt might be a determining factor for the relative fractions of two types of crystals in sPS when it is crystallized by cooling from melt. At lower $T_{\text{max}} = 310°C$ or so, both α″- and β′-crystals could be found in sPS melt-crystallized at temperatures of 230–250°C, with the β′-type becoming the only dominant species only at 260°C or higher [10,13].
Fig. 1. X-ray diffraction spectra of the neat sPS sample melt-crystallized at different isothermal temperatures from $T_{m_{ax}} = 280^\circ C$. $T_c = (a)$ 230, (b) 240, (c) 250 and (d) 260$^\circ C$, respectively.

Fig. 2. X-ray diffraction spectra of the neat sPS sample melt-crystallized at different isothermal temperatures from $T_{m_{ax}} = 380^\circ C$. $T_c = (a)$ 230, (b) 240, (c) 250 and (d) 260$^\circ C$, respectively.
Fig. 3. DSC traces in sPS melt-crystallized at (a) 230, (b) 240, (c) 250, and (d) 260°C for 120 min, respectively. $T_{\text{max}} = 280^\circ\text{C}$.

Fig. 3 shows the DSC traces (10°C/min) revealing only the $\alpha$-crystal in all sPS samples melt-crystallized at 230, 240, 250, and 260°C for 120 min. For the sPS crystallized at $230^\circ\text{C}$, dual melting endotherms, identified as P-II and P-IV, are apparently attributed to melting of the $\alpha''$-crystal in the sPS samples. This is a dramatically different trend from that in a regular sPS containing both $\alpha$- and $\beta$-crystals, which shows four melting peaks in all. Note that a minor endothermic peak labeled as $P_{\text{a,a}}$ is seen and shown by an arrowhead. This minor peak is attributed to annealing effect on the $\alpha''$-type crystal. We will show later that for sPS containing both types of crystals, two annealing peaks can be identified for each annealing step.

For comparison, the sPS samples in $\beta$-form ($T_{\text{max}} = 380^\circ\text{C}$, 0.5 min) were subjected to various thermal treatments and their thermal behavior was similarly characterized. Fig. 4 reveals the DSC traces in sPS melt-crystallized at 230, 240, 250, and 260°C for 120 min, respectively. For sPS melt-crystallized at (230–250°C) two melting peaks (identified as P-I and P-III) due to $\beta'$-type were found. The relative intensity of these two exothermic peaks apparently varies depending on the temperature of crystallization. Note that the X-ray evidence already proved that only $\beta'$-type existed in the sPS. Consequently, these two peaks (P-I and P-III) correspond to melting of the $\beta'$-type crystal. Again, interestingly, a minor endothermic peak labeled as $P_{\text{a,b}}$ is seen and shown by an arrowhead. This minor peak is attributed to annealing effect on the $\beta'$-type crystal. Apparently, the $\alpha$- and $\beta$-crystals displayed individual annealing peaks.

Several interesting features are noted. The melting temperatures of P-I and P-III ($\beta'$-type) are, respectively, lower than that of P-II and P-IV ($\alpha''$-type). In addition, the melting transition width of $\beta'$-type is narrower than that of $\alpha''$-type. This suggests that the lamellar thickness distribution of the $\alpha''$-type crystal is broader than that of $\beta'$-type. In addition, an exothermic peak of re-crystallization between P-I and P-III is obvious, and decreases with higher melt-crystallized temperatures. The DSC
evidence shows that re-organization might more readily occur in the β-crystal upon DSC scanning. The melting/re-crystallization/re-melting mechanism might be a plausible interpretation for the dual melting in the β-crystal [43].

3.2. Equilibrium melting temperature of α- and β-crystals

Each of the two crystal types could be isolated and singly produced by using different thermal treatments. It was of interest to measure and compare the equilibrium temperatures of these two crystal types. The equilibrium melting of α'-type was then determined by using the linear Hoffman–Weeks extrapolation as described below [44]:

\[ T_m = \left( 1 - \frac{1}{\gamma} \right) T_m^0 + \frac{1}{\gamma} T_c \]  \hspace{1cm} (1)

where \( T_c \) is the crystallization temperature, \( T_m^0 \) the equilibrium melting temperature and \( \gamma \) the lamellae thickening factor attributed to the ratio of lamellar thickness \( l \) to the thickness \( l^* \) of the nucleus at \( T_c \). In addition, the thin dimensions of the crystal and critical nucleus are [45]:

\[ l = \frac{2 \sigma_c T_m^0}{\Delta H_c(T_m^0 - T_m)} \]  \hspace{1cm} (2)

\[ l^* = \frac{2 \sigma_c T_m^0}{\Delta H_c(T_m^0 - T_c)} \]  \hspace{1cm} (3)
where \( \sigma_s \) is the fold surface interfacial free energy, \( T_m \) the melting temperature and \( \Delta H_f \) the heat of fusion. By re-arranging Eq. (2), \( T_m \) can be represented as:

\[
T_m = T_m^0 \left[ 1 - \frac{2\sigma_s}{\Delta H_f} \right]
\]

By using the refined techniques for isolating the individual crystal in sPS, the equilibrium temperatures of these two crystals have been more precisely determined [46]. Fig. 5 (data taken from Ref. [46]) shows the melting temperatures measured as a function of crystallization temperatures for the sPS containing only an isolated \( \alpha'' \)-type crystal. An extrapolation led to \( T_m^0 = 281.7^\circ C \) as estimated by linear Hoffman–Weeks extrapolation. It was found that the melting temperature exhibited a dependence as a function of supercooling (\( \Delta T = T_m^0 - T_c \)), but the heat of fusion seemed to be independent of supercooling. Thus, an average value of \( \Delta H_f \) can be determined from the plot, which shows \( \Delta H_f = 27.9 \) J/g. Similarly, the equilibrium temperature for the \( \beta \)-type crystal has been measured [46]. Fig. 6 (data taken from Ref. [46]) shows that the extrapolation for the equilibrium melting temperature of \( \beta' \)-type is also determined by using linear Hoffman–Weeks extrapolation. In addition, the measured heat of fusion at maximum crystallinity was plotted. The \( T_m^0 \) and \( \Delta H_f \) of \( \beta' \)-type sPS are estimated to be 288.7°C and 31.5 J/g, respectively. In comparison, the equilibrium melting temperature and heat of fusion of the \( \beta' \)-type crystal are greater than those of the \( \alpha'' \)-type. The \( T_m^0 \) of sPS has been earlier reported by some earlier works; however, inaccuracy might have been involved if samples of sPS containing mixed crystal forms were used. Earlier, Ho et al. [14] used linear and non-linear Hoffman–Weeks extrapolation procedures and obtained values of \( T_m^0 \) for the \( \alpha \)- vs. \( \beta \)-crystal, with \( T_{m,\alpha} = 273.1^\circ C \) and \( T_{m,\beta} = 278.6^\circ C \) (linear extrapolation, based on Refs. [44,45]) or \( T_{m,\alpha} = 298.4^\circ C \) and \( T_{m,\beta} = 306.9^\circ C \) (a non-linear extrapolation, based on the references cited therein [14]). Regardless of the methods of extrapolation, the earlier reported values are significantly different from that discussed here. It is believed that the more refined techniques of obtaining sPS samples containing the individually isolated \( \alpha \)- or \( \beta \)-crystal
Fig. 6. Linear Hoffman–Weeks extrapolation for melting temperatures as a function of crystallization temperatures in sPS of β'-crystal (data taken from Ref. [46]).

in Ref. [46] would lead to better accuracy in measuring the thermodynamic melting and heat of fusion of the individual crystal (α- vs. β'-crystal).

3.3. Effect of maximum temperature on crystal forms

Fig. 7A and B reveals the DSC traces in 240°C-melt-crystallized sPS samples that had been subjected to $T_{\text{max}} = 280$, 290 and 300°C, respectively, for 1 min. Samples of two initial forms were prepared: (A)
α-crystal sPS, and (B) β-crystal sPS. After being held in melt at different \( T_{\text{max}} \), both sets of sPS were then melt-crystallized at 240°C for 30 min prior to DSC characterization (10°C/min for all). The DSC result in diagram A (initially α-crystal sPS) shows that a lower \( T_{\text{max}} \) led to only α-crystal in sPS (Trace a and b) upon crystallization, but a higher \( T_{\text{max}} \) (e.g. 300°C) yielded a small fraction of β-crystal (Trace c) in addition to the α-crystal. Where there is only a single crystal in sPS, only a minor annealing peak (\( P_{a,a} \) and \( P_{a,b} \)) can be identified in the DSC curve (Trace b and c).

DSC characterization was also performed on the sPS containing initially the β-crystal that had been melt-crystallized (at 240°C) after \( T_{\text{max}} = 280–300°C \). The DSC traces in diagram B of Fig. 7 show that four peaks (α- and β-crystals) are observed for \( T_{\text{max}} = 280°C \). Upon increasing \( T_{\text{max}} \), P-II and P-IV (α-crystal) diminish quickly, but P-I and P-III (β-crystal) show an opposite trend. Apparently, upon crystallization at the same conditions, sPS containing initially α-crystal led to dominant growth of α-crystal, however, sPS containing initially β-crystal led to growth of both α- and β-crystals. In addition, regardless of the initial crystal form in sPS, \( T_{\text{max}} = 280°C \) or lower favors growth of α-crystal. A higher \( T_{\text{max}} \) would favor the β-crystal by depressing growth of the α-crystal.

The change in relative preference might be related to availability of residual α-crystal when held at \( T_{\text{max}} \) that is above or below the equilibrium temperature of the α-crystal. If the maximum temperature is imposed on sPS containing initially the α-crystal as nuclei, the nuclei crystal may or may not be erased completely depending on the fact whether or not \( T_{\text{max}} \) was above the equilibrium temperature (\( T^0_{\text{BD}} = 281.7°C \)) of α- type. When the maximum temperatures were below the equilibrium temperature (\( T^0_{\text{BD}} = 281.7°C \)) of α- type, growth of α-crystal was kinetically favored and only P-II and P-IV dual peaks were found in the 240°C-crystralized sPS sample when scanned in DSC. On the other hand, a higher \( T_{\text{max}} \) might erase the residual α-crystal nuclei, completely or partially. In that case, the growth of α-crystal becomes less kinetically favored. Instead, both α- and β-crystals can be grown simultaneously, whose relative rates depend on the temperature of crystallization. In the extreme case of either a high \( T_{\text{max}} \) or high \( T_{\text{c}} \), only the β-crystal could be produced in sPS upon melt crystallization.

It was necessary to explore whether or not the time duration (residence time) in melt at \( T_{\text{max}} \) might have an effect. The growth of the α- type crystal might be inhibited in sPS if held on the melt for a longer time. Fig. 8 shows the DSC trace (10°C/min) for a 240°C-melt-crystallized sPS sample (containing initially α-crystal), which had been previously heated to \( T_{\text{max}} = 300°C \) for 30 min prior to being cooled for crystallization at 240°C. Apparently, for time up to 360 min at \( T_{\text{max}} \), the intensities of P-II and P-IV (α-crystal) are about comparable with those in the sPS held at the same \( T_{\text{max}} \) but for a shorter time (1 min), shown in the previous figure (Fig. 7A, Trace c). As long as \( T_{\text{max}} \) remained the same, a longer residence time in the melt did not seem to erase more of the α- type nuclei, or led to growth of only the β-crystal. Thus, a longer residence time is not a related factor to which the β- type is preferred. The polymorphism in sPS is quite independent of the residence time in the molten state at \( T_{\text{max}} \).

The α- type is presumed to be a kinetically more accessible crystal, while the β- type is of a thermodynamic stable crystal packing [9–14]. Thus, it is hypothesized that α- type crystal might proceed with higher crystallization rates. This is indeed the case even when the sPS (initially quenched to a glassy state) is subjected to a very high \( T_{\text{max}} = 380°C \), which is high enough to erase any trace nuclei. Fig. 9 shows the DSC thermograms (10°C/min) for the sPS samples (initially quenched to a glassy state then soaked at \( T_{\text{max}} = 380°C \), 0.5 min) melt-crystallized at several isothermal temperatures: 230, 240, 250 and 260°C, respectively, for 120 min at each of the isothermal temperatures. Multiple peaks are evident for all samples; however, the sPS sample melt-crystallized at the lowest temperature of
230°C exhibited four peaks, suggesting simultaneous existence of two crystal types. The sPS sample, melt-crystallized at the highest temperature of 260°C, exhibited only one peak labeled as P-I (which is now elevated owing to thickened lamellae) that is attributed to only the β-crystal. In between these two samples (crystallized at the lowest and highest temperatures, respectively), a clear trend of peak shifting
and merging is apparent for the other sPS samples of ascending order (240 and 250°C). P-I and P-III become greater in intensity with increasing temperatures of crystallization. Finally, P-II and elevated P-I become merged into a single peak for the 260°C-crystallized sPS. Note that the P-II and P-IV due to \( \alpha'' \)-type are present in sPS melt-crystallized at 230, 240, and 250°C, but absent during the 260°C-crystralization. This result suggests that for the extremely high \( T_{\text{max}} = 380°C \) (0.5 min), the \( \alpha'' \)-type could still be found as long as the crystallization proceeded at fast rates, e.g. for the sPS melt-crystallized at low temperatures of 230 or 240°C. However, only \( \beta' \)-crystal was found when melt-crystallized at a high temperature of 260°C, where nucleation and growth rates were low. Obviously, the result suggests that the \( \alpha'' \)-type is a kinetically favored crystal if crystallization proceeds at lower temperatures and higher rates.

Fig. 10 demonstrates the DSC thermograms (10°C/min) for the sPS samples melt-crystallized at several isothermal temperatures: 230, 240, 250 and 260°C, respectively, all for 120 min, after having been subjected to a molten state of \( T_{\text{max}} = 280°C \) (1 min). Again, prior to the DSC characterization, the initial sPS was obtained by solution-casting, which thus contained the \( \beta(\beta') \)-crystal. Similarly, four melting peaks labeled as P-I, P-II, P-III, and P-IV were observed when crystallized at 230°C. A combination of \( \alpha'' \) - and \( \beta' \)-crystals coexist regardless of melt crystallization temperatures in sPS. Thus, it demonstrates that even the initial material contained isolated \( \beta' \)-type crystal (sPS cast from solution), it could yield \( \alpha'' \)-type during melt crystallization as long as \( T_{\text{max}} \) or \( T_c \) is low. Apparently, for this sample, the \( \alpha'' \)-type was also found in sPS even when subjected to a very high \( T_{\text{max}} \). The initially present crystal forms in sPS influence the polymorphism. The sPS containing initially \( \alpha'' \)-type (quenched glassy sPS) leads to preferential \( \alpha'' \)-type packing, while sPS initially comprising the \( \beta' \)-type crystal (cast from a solution at 160°C) favors crystallization leading to the \( \beta' \)-type, especially in cases where \( T_{\text{max}} \) is low.

![Figure 10](image-url)

**Fig. 10.** DSC thermograms (10°C/min) for the sPS samples melt-crystallized at several isothermal temperatures: (a) 230, (b) 240, (c) 250 and (d) 260°C, respectively, all for 120 min at each of the isothermal temperatures. \( T_{\text{max}} = 280°C \) (1 min).
Table 1
Melt crystallization of α-crystal (initial form: quenched sPS; $T_{max} = 280^\circ C (1 \text{ min}), \text{ Ave}: n = 1.5 \pm 0.1$ (α-crystal only))

<table>
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<th>$n$</th>
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3.4. Crystallization kinetic analysis of α- vs. β-forms

Crystallization leading to the α-crystal proceeds with higher crystallization rates, with possibly unsuppressed nuclei. On the other hand, crystallization at higher temperature and lower rates leads more easily to the β-crystal in sPS. Hence, it was of interest to investigate and compare the crystallization kinetics of individual α- vs. β-crystals. The classic Avrami equation used for analysis is [47]:

$$1 - X_i = \exp[-k t^n]$$

where $k$ is the crystallization rate constant depending on nucleation and growth rate; and $n$ is the Avrami crystallization exponent depending on the nature of nucleation and growth geometry of the crystals. $X_i$ is the relative crystallinity of the polymer sample at time $t$, defined as the ratio of the cumulative area under the exotherm peak up to $t$, $\Delta H_c(t)$ with respect to the total peak area of the crystallization exotherm, $\Delta H_c$, in the DSC curves. That is, $X_i = \Delta H_c(t)/\Delta H_c$. Only the data of $X_i$ between 10 and 50% were used in analysis for simplification.

Crystallization kinetics of individual α- vs. β-crystal in sPS has been analyzed in a recent paper [46]. The measurement of individual α- vs. β-crystal crystallization involved a refined technique of preparing sPS so that it contained isolated α- or β-crystal discussed in Ref. [46]. The kinetic values of $n$ and $k$ for the melt crystallization of individual α-crystal, β-crystal, or mixed α- and β-crystals in sPS are tabulated and compared in Tables 1–4. The average value of $n$ equal to 1.5 for the α-crystal (upon melt crystallization) apparently indicates a heterogeneous nucleation mechanism with diffusion control. The heterogeneous nucleation suggests that crystal growth is faster and the nuclei are simultaneously present at the initiation of crystallization. Consequently, the crystallization of the α$''$-type is kinetically more accessible.

Table 2
Melt crystallization of β-crystal (initial form: solvent cast sPS; $T_{max} = 380^\circ C (1 \text{ min}), \text{ Ave}: n = 2.5 \pm 0.1$ (β-crystal only))

<table>
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addition, the value of $k$ decreases with higher temperatures of melt crystallization. This manifests that the crystallization rate becomes lower with increasing melt crystallization temperatures. By comparing the $k$ values for these two types, it is found that the growth rates of the $\alpha''$-type are faster than that of $\beta'$-type under the same melt crystallization temperatures. The crystallization kinetics for the $\beta'$-crystal sPS is significantly different. The value of $n = 2.5 - 2.6$ suggests that the crystal growth in the $\beta'$-crystal in sPS is of homogeneous nucleation and the growth pattern is 3-D spherical, which is the main crystallization mechanism of melt crystallization at high temperatures. X-ray diffraction analysis has confirmed that indeed the $\beta'$-type is the main crystal produced in high-temperature melt-crystallized sPS samples. Note that melt crystallization of sPS at intermediate temperatures lead to co-existing $\alpha$- and $\beta'$-crystal. Generally, melt crystallization at low temperature favors the $\alpha$-crystal while high temperature favors the $\beta'$-crystal. Melt crystallization (Tables 3 and 4) of sPS containing mixed $\alpha$- and $\beta'$-crysals is similar to the characteristic of the $\beta'$-crystal, which is attributed to the major fraction of the $\beta'$-crystal in sPS. The exponent differs by about 1.0 for the $\beta'$- vs. $\alpha$-crystal crystallization kinetics, which may be originate from the nucleation mechanisms. The heterogeneous nucleation suggests that crystal growth is faster and the nuclei are simultaneously present at the initiation of crystallization.

Fig. 11 depicts the optical micrographs showing tiny spherulites of sPS melt-crystallized at (A) 230 and (B) 260°C (pre-soaked at $T_{\text{max}} = 280°C$, 1 min), which contained only the $\alpha$-crystal. Both optical microscopy results confirmed that the crystallization kinetics of the $\alpha$-crystal sPS is of a heterogeneous nucleation, which remained so regardless of melt crystallization temperatures (230–260°C). By contrast, Fig. 12 shows the optical micrographs for the spherulites of sPS melt-crystallized at (A) 230 and (B) 260°C (pre-soaked at $T_{\text{max}} = 380°C$, 0.5 min), which contained only the $\beta'$-crystal. Large spherulites

<table>
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Fig. 11. Optical micrographs showing highly-nucleated, tiny spherulites in sPS of α-crystal.

Fig. 12. Optical micrographs showing large impinged spherulites in sPS of β-crystal.
with significant impingement are the major morphology feature for the 230°C-crystallized sPS (Graph A). When crystallized at a higher temperature of 260°C, the spherulites exhibited a sheaf-like pattern (Graph B), suggesting coarsening of the lamellae. This comparison in the optical evidence for the α- vs. the β-crystal demonstrates that β"-crystal grows with crystallization kinetics in homogeneous nucleation, leading to fewer nuclei density, slower rates, but much larger spherulites. By contrast, the faster rates and higher nuclei density in the crystallization of the α-crystal are a main feature for the heterogeneous nucleation, and such crystallization results in tiny spherulites.

3.5. Effect of miscibility on polymorphism

In contrast with the fact that both α"- and β'-types usually co-exist in melt-crystallized neat sPS, only the β-type is identified in miscible sPS/aPS or sPS/PPO blends [9, 11, 13, 20–22]. Actually, however, the α-crystal in addition to the β-crystal could also be grown in miscible blends of sPS; but the relative fractions of α- and β-crystals are quite different from those in a neat sPS when all were crystallized at the same conditions. Apparently, factors related to the miscibility might have influenced the polymorphism in sPS.

For investigating the factors influencing the polymorphism in the miscible sPS/aPS blend system, three compositions of sPS/aPS blends samples were prepared: 75/25, 50/50, and 25/75, with each starting as quenched glass material, melted at various \( T_{\text{max}} \) for 1 min. Finally, the blend samples were cooled to a fixed 230°C isothermal temperature for 30 min crystallization. DSC characterization was then performed to evaluate the changes in polymorphism and melting behavior. Fig. 13 shows the DSC thermograms (10°C/min) revealing multiple endothermic peaks of the sPS/aPS blends of three compositions: (A) 75/25, (B) 50/50 and (C) 25/75. In Diagram A (for sPS/aPS, 75/25), DSC Trace a and b (low \( T_{\text{max}} = 275, 280^\circ\mathrm{C} \)) show two peaks identified as P-II and P-IV attributed to existence of the only α"-type crystal. Trace c (for high \( T_{\text{max}} = 300^\circ\mathrm{C} \)) displays three peaks labeled as P-I, P-II and P-III, which reflect melting of a combination of α"- and β'-crystals. In Diagram B, for the sPS/aPS (50/50) blend,
Trace a (low $T_{\text{max}} = 275^\circ\text{C}$) shows two melting endotherms attributed to $\alpha''$-type, while Traces b and c ($T_{\text{max}} = 280$ and $300^\circ\text{C}$) exhibit three peaks for melting of $\alpha''$- as well as the $\beta'$-crystal. Apparently, a lower $T_{\text{max}}$ led to more and more $\alpha''$-crystal while a high $T_{\text{max}}$ resulted in only $\beta$-crystal in sPS/aPS blend when melt-crystallized at the same conditions. In Diagram C, for sPS/aPS blend of 25/75, three peaks attributed to the melting of co-existing $\alpha''$- and $\beta'$-crystals are observed regardless of the maximum melting temperatures ($T_{\text{max}} = 275, 280$, or $300^\circ\text{C}$). This suggests that at high amorphous aPS contents in sPS/aPS, the $\alpha$-crystal nuclei are erased in larger extents even at low $T_{\text{max}}$, causing a stronger inhibition of the $\alpha$-crystal and consequently, a better chance for the $\beta$-crystal to grow. Therefore, the $\beta$-crystal (along with the $\alpha$-crystal) is seen in the sPS/aPS (25/75) sample, but not in sPS/aPS (50/50 or 75/25) samples, where only the $\alpha$-crystal exists.

3.6. Relative stability of $\alpha$- vs $\beta$-crystals in neat sPS

Possible types of irreversible melting for sPS at constant pressure can be described by referring to a schematic diagram constructed by using similar concepts illustrated in the literature [48]. Fig. 14 shows the free energy vs. temperature depicting the equilibrium and metastable states of various crystals in the neat sPS and its miscible blends with aPS. The bold curves (or lines) represent the free energies of the equilibrium crystal and melt. The thin curves (or lines) represent states of higher free energy attributed to metastable crystals (or unstable crystals). The plot can be used to explain a few experimental results. In previous papers, a sample originally in the $\delta$-form is subjected to successive increases of the temperature of 20°C in the range 60–200°C. It has been found that in conditions where a sample containing the $\delta$-form subjected to successive increases of the temperature of 20°C in the range 60–200°C, a $\gamma$-crystal can be seen at above 140°C and a $\alpha'$-form above 200°C [6]. In addition, transformation from the $\delta$-crystal to $\beta''$-type has been reported in sPS samples when annealing at 160°C directly. Recent studies have pointed out that a mesophase with helical conformation can be obtained by removing the solvent during heating from the $\delta$-type extracting from a solution with acetone at 60°C [6–8]. The mesophase with all zig-zag $\text{trans}$-conformation can also be obtained by annealing a quenched glassy sPS at above the glass transition temperature. Upon melt crystallization, a combination of both $\alpha''$- and $\beta'$-type are generated. Upon cold crystallization, only $\alpha$-crystal ($\alpha'$ and $\alpha''$) and no $\beta$-crystal is generated with the $\alpha'$-type forming at temperatures below 200°C and the $\alpha''$-type generated at temperatures above 200°C in neat sPS.

In the miscible sPS/aPS blend (as well as miscible sPS/PPO blend), it was found that $\beta'$-type was preferred for crystal packing while the $\alpha$-crystal growth was much inhibited unless the sPS/aPS blend was crystallized at comparatively lower temperatures or pre-soaked at low $T_{\text{max}}$. Thus, the $\beta'$-type possesses a lower free energy (and thus more stable) than other crystals. When all other conditions were held the same, the fraction of $\beta'$-type crystal increased with increasing aPS contents in the sPS/aPS blend, but the $\alpha''$-type showed an opposite trend. This evidence demonstrates that $\beta'$-type is preferred for packing in miscible sPS/aPS blends with high aPS contents. As mentioned earlier, it may be possible that the factors are related to miscibility/interactions between sPS and aPS. One main issue may be the relative changes of the equilibrium melting temperatures of sPS in blends with respect to $T_{\text{max}}$. For miscible semi-crystalline/amorphous polymer, the amorphous molecular chain segments would reduce the melting temperatures of neat semi-crystalline polymer according to the Flory–Huggins relationship [49]. The value of $\chi$ in sPS/aPS blends is $-0.11$ [50], leading to binary miscibility in sPS/aPS blends. Thus, for miscible mixture of sPS and aPS, the equilibrium melting temperatures corresponding to the
\( \alpha'' \)- and \( \beta' \)-type can both be reduced because of the favorable molecular interactions. Since the equilibrium melting temperature of \( \alpha'' \)-type is always lower than that of \( \beta' \)-type even in mixture of sPS/aPS. Thus, at above the equilibrium melting temperatures of \( \alpha'' \)- and/or \( \beta' \)-type sPS, the \( \beta' \)-type exhibits a more stable state with the normal polymer liquid. Furthermore, the polymer pairs in the sPS/aPS blends form a thermodynamically more stable solution than that in neat sPS. This indicates that even at a lower
temperature of 280°C of residence in the molten state, the major \( \beta' \)-type (regarded as P-I and P-III crystal lamellae) are formed during melt crystallization of 230°C in the sPS/aPS blends, for two blend compositions of 50/50 and 25/75. In comparison with the neat sPS quenched to a glassy state, the \( \beta' \)-type forms more easily in the sPS/aPS blend mixtures. In addition, it was also found that the crystallization rate decreased with increasing aPS contents; thus, a lower crystallization rate favors growth of \( \beta' \)-crystal. Two main factors, i.e. lowered equilibrium melting points and lowered crystallization rates, as discussed before may be responsible for the formation of \( \beta' \)-type and inhibition of \( \alpha'' \)-type in the miscible blends. The equilibrium melting points of both the \( \alpha \)-and \( \beta \)-crystals are reduced in the sPS/aPS blend, especially so at high aPS contents. Therefore, it leads to a fact that the \( \alpha \)-crystal nuclei could be more readily erased when held at a fixed \( T_{\text{max}} \). The growth of \( \alpha \)-crystal is highly dependent on nuclei of \( \alpha \)-crystal. Its growth, therefore, becomes less favorable at higher aPS contents or higher \( T_{\text{max}} \).

3.7. Relationships between polymorphic crystals and multiple melting

Both \( \alpha'' \)- and \( \beta' \)-crystals co-exist in a melt-crystallized sPS (processed with normal thermal schemes). It was critical to investigate whether each of the \( \alpha'' \) - and \( \beta' \)-crystals might individually display dual (or multiple) melting behavior. A series of questions have to be answered. Can the \( \alpha'' \)-type be transformed to the \( \beta' \)-type, or vice versa? If there is a transformation of \( \alpha'' \) - and \( \beta' \)-type, is it via a solid–solid transformation? Or, is it via a route that the previous crystal is first melted during a thermal treatment (scanning or heating to an isothermal temperature) and then re-crystallized to another crystal type (i.e. a solid–liquid–solid rather than a direct solid–solid transformation)?

Fig. 15 reveals the DSC traces for the sPS (containing \( \alpha'' \)-type) samples melt-crystallized at 240°C for

![DSC thermograms](image)

**Fig. 15.** DSC thermograms (10°C/min) for sPS of \( \alpha'' \)-type 240°C-melt-crystallized for various times ranging from 30 to 1560 min.
Fig. 16. X-ray diffractograms of sPS melt-crystallized at 240°C for 240 and 1560 min, respectively.

various times from 5 to 1560 min. Interestingly, P-II is shifted to high temperature with increasing isothermal times while the intensity of P-IV is diminished and its temperature is constant. Finally, only an elevated P-II, which is merged as a diminished P-IV is observed in the sample annealed for a longer time of 1560 min.

X-ray analysis can be used to investigate the polymorphism of sPS for discerning the α''- and β'-crystal. Fig. 16 shows the X-ray diffractograms of sPS samples melt-crystallized at 240°C for: (bottom) 240 min, and (top) 1560 min, respectively. It is seen that only diffraction peaks attributed to α''-type are present without β'-type crystal regardless of annealing times. The X-ray evidence suggests that no solid–solid transformation of α''-type to β'-type occurs during longer times of residence at a melt crystallization temperature of 240°C. Interestingly, as the P-II peak shifts to a higher temperature, the P-IV intensity decreases. This demonstrates that the pre-existing thin lamellae attributed to P-II can be further thickened with longer annealing times. As a result of continuous thickening of the P-II lamellae, the amount available for re-organization into the P-IV species becomes gradually less, which was evidenced by the fact that greater intensity in P-II and less intensity in P-IV was observed in samples subjected to long annealing at all temperatures.

Possible effects of heat scanning or annealing on transformation of crystal types (e.g. from α-crystal to β-type) were examined. Three sPS samples subjected to different thermal treatments: (a) melt-crystallized at 240°C for 30 min, (b) melt-crystallized at 240°C (30 min), scanned to 270°C (10°C/min), or (c) melt-crystallized at 240°C (30 min), then scanned to 270°C, held for 120 min. The sPS starting material was prepared in such a way that it contained initial α-crystal and T_{max} = 280°C for 1 min. X-ray characterization was performed on the samples. Fig. 17 shows (A) the X-ray results for samples a–c, which is placed side-by-side with the DSC result, (B) melting behavior of sample a–c. The X-ray result revealed that only α''-crystal characteristic peaks are seen, suggesting that the previously present α''-type remained to be the α''-crystal and no transformation to the β'-crystal was observed. The DSC result also revealed that the α-crystal is the only species in all samples. Upon thermal scans or annealing treatments, the relative intensities of P-II and P-IV changed, but the melting peaks reflected that only α-crystal was present and no traces of β-crystal was found.
Fig. 17. X-ray diffractograms of α-crystal sPS subjected to several thermal treatments: (a) melt-crystallized at 240°C for 30 min, (b) then after scanning to 270°C at a scan rate of 10°C/min, cooled to room temperature, or (c) annealed at 270°C for 120 min directly.

Similarly, possible effect of heat scanning on transformation of crystal types from the β-crystal to the α-type (or vice versa) was examined. The starting sPS material contained solvent-induced β"α"-type, subjected to \( T_{\text{max}} \) at 380°C for 0.5 min. Samples were prepared in such a way that they contained only the β-crystal, and the samples were then subjected to various thermal treatments to examine whether or not the pre-existing β-crystal might be altered to a different crystal form. sPS samples were subjected to several thermal treatments: (a) melt-crystallized at 240°C for 30 min, (b) then after scanning to 263°C at a scan rate of 10°C/min, cooled to room temperature, or (c) annealed at 263°C for 120 min. In addition, the corresponding thermal behaviors of these samples were characterized. Fig. 18 shows the (A) X-ray diffractograms of these three samples (a–c), which are placed side-by-side with the DSC result, (B) melting behavior of samples a–c. The X-ray result showed that only the β-crystal was found in all samples, which suggests that no alteration of crystal forms (e.g., from β- to α-form) upon DSC scanning was observed. The DSC result also revealed that the β-crystal is the only species in all samples. Upon thermal scans or annealing treatments, the relative intensities of P-I and P-III changed, but the melting peaks reflected that only the β-crystal was present and no traces of α-crystal were found.

3.8. Identification of crystal forms and spherulites in cold-crystallized sPS

Cold crystallization means that the sPS polymer crystallizes not from a molten state but from an amorphous glassy rubber, which is in a state of higher rigidity, less flexibility, and thus less randomness, than from a melt liquid state. For most semicrystalline polymers with only a single crystal unit cell, melt- and cold crystallization would produce different spherulites but the same unit crystal cell. sPS, which
Fig. 18. X-ray diffractograms of β-crystal sPS samples subjected to several thermal treatments: (a) melt-crystallized at 240°C for 30 min, (b) then after scanning to 263°C at a scan rate of 10°C/min, cooled to room temperature, or (c) annealed at 263°C for 120 min.

possesses capability of packing into different crystal cells, can develop different crystal forms (as well as different spherulite sizes) upon different crystallization conditions. More interestingly, cold-crystallized sPS would generate different crystal forms as well as significantly different spherulite morphology than those found in the melt-crystallized sPS. It has been proven that neat sPS develops predominant α-cell packing when cold-crystallized at any temperature [10]. Cold-crystallized sPS differs significantly from melt-crystallized sPS in the crystal forms and melting behavior [10]. It has been pointed out that cold-crystallized sPS is packed primarily by α-type unit cell, while melt-crystallized sPS is packed by mixed fractions of both β- and α-type unit cells depending on temperature of crystallization (Tc), maximum soaking temperature (Tmax) at molten state prior to rapidly quenching to melt crystallization [13]. In addition to the difference in unit cells, the lamellar/spherulitic morphology also differs significantly between the cold-crystallized sPS [26] vs. melt-crystallized one.

The melting behavior and stability of these two crystal types (α, β) are likely different. Under same thermal histories, the α-type crystal melts at higher temperatures than the β-type. Kinetically, the growth of α-crystal lags behind β-type as the molten sPS is brought to a super-cooled state to initiate crystallization. When just freshly cooled from the molten state, most sPS molecules possess sufficient mobility and the β-crystal initially is the main mechanism of packing during melt crystallization at high temperatures. This is to be followed by α-type crystal packing during later stages of melt crystallization in a partially solidified sPS system where packing of β-form is more inhibited. This suggests that the α-type crystal becomes an alternative mechanism of molecular packing for partially solidified sPS, in which most chains are stiffened or possess a reduced molecular mobility owing to partial crystallinity or solidification. Melt crystallization in sPS, thus, leads to co-existing α- and β-crystals of different fractions depending on temperature.
Similar view is taken in discussing the cold-crystallized sPS. In situation of cold crystallization where the sPS molecules are being organized into crystals from an originally rubbery state, the α-crystal is the dominating mechanism of molecular packing as the rubbery sPS chains are comparatively less flexible (or more sluggish) than the molten sPS chains in the liquid state. Furthermore, it has been proven that the lamellae of β-crystal can be thickened upon annealing or re-melted/re-crystallized into thicker lamella during scanning at slow heating rates; by comparison, lamellae of α-crystal cannot be thickened [9–13]. When the α-crystal is melted during heating scans, the experimental evidence shows that it does not re-organize into thicker lamella. It simply melts into liquid without re-crystallization upon further heating.

X-ray crystal analysis has been performed on cold-crystallized sPS samples to indicate that the α-form crystal (hexagonal unit cell) is the dominant crystalline domain, with two α-crystal sub-forms (α' and α''-crystals) [26]. High temperatures favors the α''-crystal and lower temperatures tend to favor the formation of the α'-crystal (<175°C). Fig. 19 (data taken from Ref. [26]) shows X-ray diffractograms for sPS cold-crystallized at (a) 175, (b) 200, and (c) 260°C, respectively, for 120 min. The result shows that only α-form crystal is present. Depending on crystallization temperatures, the α-form can be sub-divided into two minors: α'-crystal at temperatures below 175°C and α''-crystal at temperatures above 200°C. The samples cold-crystallized at lower temperatures (i.e. 150 and 175°C) exhibited three diffraction peaks at 2θ = 6.7, 11.8, and 18.0°, which are α'-form according to De Rosa et al. [6]. But the sPS samples cold-crystallized at higher temperatures of 200, 225, 250, or 260°C exhibited sharper diffraction peaks at 2θ = 6.8, 10.3, 11.7, 14.0, 15.6 and 17.0 and 20.2°, which are typical of α''-crystal [6]. The peak at 20.2° is characteristic of α- and β-forms and is present regardless of thermal treatment. All characteristic peaks of the β-crystal (2θ = 6.1, 10.4, 12.3, 13.6, 18.6, 20.2, 21.3 and 23.9°) are absent from the cold-crystallized sPS.

![Fig. 19. X-ray diffractograms for sPS cold-crystallized at (a) 175 (b) 200, (c) 250 and (d) 260°C, respectively, for 120 min (data taken from Ref. [26]).](image-url)
IR spectroscopy has also been used to confirm that α′-crystal is favored at lower temperature cold crystallization (175°C), but a combination of α′- and α″-crystals co-exist at medium temperatures (200°C), while only α″-crystal could be obtained when cold-crystallized at higher temperatures above 225°C [26]. Fig. 20 (data taken from Ref. [26]) displays the FT-IR spectra of sPS cold-crystallized at (a) 150, (b) 200, and (c) 260°C for 120 min, respectively. For the cold-crystallized sPS, a peak at 1222 cm⁻¹ was clearly seen, which is associated with α-crystal molecular chain trans-skeletal conformation [29–30,51–54]. For the cold-crystallized sPS samples, a sharper peak at 901.7 cm⁻¹ (adjacent to the 905.5 cm⁻¹ peak) was seen, which is indicative of α-crystals. Additionally, for the sPS cold-crystallized at 200°C, there are two small but distinct peaks located at 856.8 and 852 cm⁻¹, respectively, indicating the characteristic absorption peaks related to the α′ and α″-crystals [51,52].

DSC analysis has been performed to reveal the unique thermal characteristics of cold-crystallized sPS [26]. Fig. 21 (data taken from Ref. [26]) shows DSC thermograms for sPS cold-crystallized at isothermal temperatures: (a) 150, (b) 175, (c) 200, (d) 225, (e) 250°C, all for 30 min, and (f) 260°C for 120 min, respectively. Evidently, the thermal behavior as seen in the DSC thermograms, exhibits a continuous trend of variation depending on the temperature of cold crystallization imposed on the samples. In general, as the cold crystallization temperature increases, the breadth of the melting peaks (as indicated by the double-arrow range) decreases. A rather broad endothermic melting peak is observed when crystallized at 150–200°C. Furthermore, the melting behavior of the crystals in sPS cold-crystallized at higher temperatures (225–260°C) is seen to be significantly different from the sPS sample cold-crystallized at 150°C. sPS crystallized at temperatures between 175 and 200°C exhibits a broad melting peak superimposed with a minor but sharper shoulder endothermic peak. At higher temperatures of cold crystallization, the sharper peak rapidly shifts to a higher temperature.
A revealing difference in the spherulitic morphology of cold-crystallized sPS was found in examining the lamellar structure by using POM and/or SEM [26]. Fig. 22 (data taken from Ref. [26]) shows the SEM morphology for the sPS samples of different cold crystallization treatments at (A) 150°C, (B) 225°C, and (C) 260°C, all for 120 min. Graph A shows the morphology in sPS cold-crystallized at 150°C, revealing small granular crystallites of less than 80 nm. Unlike regular spherulites grown from the molten state, no bundles of lamellae were found (or visible) inside the granular spheres of cold-crystallized sPS. On the other hand, Graph B shows that post-development of lamellar morphology surrounding the tiny spherules was observed if the sPS was cold-crystallized at increasingly higher temperatures (225°C). At even higher temperatures, cold-crystallized sPS exhibits distinctly different morphologies. The SEM Graph C shows that sPS samples, cold-crystallized at 260°C for 120 min, develop a peculiar morphology consisting of tiny crystals in the spherical center with secondary lamellae radiating out from the spheres.

A direct comparison might help in examining the differences between the melting behavior of the sPS samples that are cold- and melt-crystallized, respectively [10]. Fig. 23 (data taken from Ref. [10]) displays the DSC traces (a,b), showing the melting peaks for three sPS samples: (a) melt-crystallized, and (b) cold-crystallized at 240°C, 30 min, respectively. The melt-crystallized (240°C, 30 min) sPS exhibits three melting endotherms: $T_1 = 260°C$, $T_2 = 265°C$, $T_3 = 272°C$ for Peak-I, P-II, and P-III. There is apparent dramatic difference between the melt-crystallized sPS samples and the cold-crystallized sPS (Thermogram-b). The melt-crystallized sample upon scanning exhibited three distinct and sharp peaks, which are located at $T_1 = 260$, $T_2 = 265$, and $T_3 = 272°C$, respectively. By comparison, the cold-crystallized sample displays a single merged peak (269°C), regardless of the temperature at which cold crystallization took place. The single, but broad-based, peak for the cold-crystallized sample is likely to be merged signal of several close-spaced melting peaks.

Effects of higher temperatures (higher than 240°C) and/or more extended time (longer than 30 min) of
Fig. 22. SEM morphology for the sPS samples of different cold crystallization treatments at: (A) 150°C, (B) 225°C, and (C) 260°C, all for 120 min (data taken from Ref. [26]).

Fig. 23. DSC traces (a, b) showing the melting peaks for three sPS samples: (a) melt-crystallized, and (b) cold-crystallized at 240°C, 30 min, respectively (data taken from Ref. [10]).
melt crystallization were investigated by comparing the sPS samples subjected to melt crystallization at two different temperatures or times. Fig. 24 (data taken from Ref. [10]) shows the DSC traces of melting peaks of sPS samples melt-crystallized, respectively, at (a) 240°C for 30 min and (b) 250°C for 30 min. The melt-crystallized sample upon scanning (at 5°C/min) exhibited four, three, two or only one distinctly sharp peak(s) depending on the temperature of melt crystallization. Apparently, melt crystallization at 250°C led to the fact that the peak temperatures of Peak-I (at 266°C) and Peak-II (271°C) were significantly elevated (by 6°C) in comparison to those (P-I = 260°C, P-II = 265°C) of sPS melt-crystallized at 240°C.

It has been earlier reported [9] that for the melt-crystallized sPS sample, three peaks are clearly seen, which are labeled as Peak-I, P-II, and P-III, respectively. The assignment of melting peaks (Peaks 1–3) to possible crystal forms follows the analyses in previous reports [9]. There has been less disagreement in the point that melting peak P-I is attributed to the β-crystal, while P-II is related to the α-type. In general, for melt-crystallized sPS samples, subjected to further annealing at higher temperatures, a certain fraction of the originally existing α-type (P-II) may be transformed to the β-type (P-I) but not vice versa. This was further evidenced by DSC traces that for the melt-crystallized sPS samples annealed at a high temperature (between 240 and 260°C) for extended time; the intensities of P-II is diminished (α-type), while the intensity of P-I (β-type) is increased and elevated to a higher temperature.

Interestingly, upon crystallization at an even higher temperature (e.g., 260°C) for a long time of 120 min, the thermal behavior of melt-crystallized sPS displays only a single sharp melting peak [10]. Fig. 25 (data taken from Ref. [10]) is the DSC result for the sPS melt-crystallized at 260°C upon scanning, which shows only a greatly intensity-enhanced and temperature-elevated P-I ($T_m = 272°C$). From these trends of peak shifting, it further indicates that P-I may be associated with the β-form crystal.
3.9. Effects of tacticity and molecular weight

It has been found that the sPS of lower molecular weights and/or lower tacticity ($M_w = 63,000$ g/mol) developed only $\beta$-crystal when held for melt crystallization at any temperatures [55]. This is quite interesting and surprising. Usually, when sPS of high molecular weights and high tacticity is melt-crystallized at most medium temperatures (230 - 250°C), the crystals are packed with both $\alpha$- and $\beta$-crystal unit cells with various fractions, which depend on factors, such as temperature, cooling rate, or other thermal histories [13]. Molecular weight apparently has an effect on relative fractions of $\alpha$- vs. $\beta$-crystals in sPS upon melt crystallization. Nevertheless, cold crystallization of sPS of any molecular weight leads only to the $\alpha$-crystal [10,26]. By using the sPS model of a low molecular weight ($M_w = 63,000$ g/mol), relationships between the polymorphism and melting behavior in the melt-crystallized sPS, containing only the $\beta$-crystal, are briefly discussed.

Fig. 26 (data taken from Ref. [55]) shows (A) SEM graph, along with (B) DSC trace for the sPS sample subjected to melt crystallization at 230°C for 2 h. The DSC trace (diagram B) for this sPS sample (melt-crystallized at 260°C) shows melting peaks of P-I, P-II, and P-III. The straight lamellar bundles (thin, flat-on lamellae) in sPS melt-crystallized at 230°C are likely to be the crystal species that yields the P-I melting peak. The lamellar platelets resembling twin eyes are crystalline domains representing the thicker species of lamellae, whose melting is denoted by the P-II endotherm. Note the P-III crystal species (the thickest lamellae) were not initially present in a significant quantity in the 230°C-melt-crystallized sPS. The P-III peak as revealed in the DSC thermogram by heat scanning the 230°C-melt-crystallized sPS simply indicates a sum of the originally present P-III and transformation of the melted P-I and P-II species and repacked into additional P-III crystal upon DSC scanning. Therefore, for the 230°C-melt-crystallized sPS sample (only melt-crystallized but not post-heated or scanned), the SEM graph shows clearer evidence of P-I and P-II crystal entities, but less indication of the thickened P-III crystal.
Fig. 26. Morphology in direct correlation with thermal behavior for sPS samples melt-crystallized at 230°C for 2 h: (A) SEM graph, (B) DSC trace (5°C/min) (data taken from Ref. [55]).

When melt-crystallized at higher temperatures, sPS exhibits significantly different melting behaviors and morphologies [55] from those melt-crystallized at lower temperatures. Fig. 27 (data taken from Ref. [55]) shows (A) SEM graph, along with (B) DSC trace for the sPS sample subjected to melt crystallization at 260°C for 2 h. As discussed earlier, the crystalline morphology apparently contains only thickened, highly-branched edge-on lamellar crystal of P-III. Note that the P-III lamellae are now indistinguishable from the annealing-thickened P-I crystal. That is to say, upon melt crystallization at 260°C, P-I is thickened to such an extent that its endotherm is superimposed with the P-III crystal upon DSC scanning. The characteristic morphology patterns of initial P-II and P-I crystals are virtually not seen. The DSC trace (diagram B) for this sPS sample (melt-crystallized at 260°C) shows only melting peak of P-III. In summary, for the sPS sample melt-crystallized at 260°C or above, the morphology shows only highly branched, edge-on lamellae (P-III). Very few platelet lamellae (P-II) and almost no flat-on lamellar bundles (P-I) are visible at all; that is, P-III crystal is the only dominating species. In summary, for the sPS sample melt-crystallized at 260°C or above, the morphology shows only highly branched, edge-on lamellae (P-III). Very few platelet lamellae (P-II) and almost no flat-on lamellar bundles (P-I) are visible at all. That is, P-III crystal is the only dominating species. The corresponding thermal behavior bears a strikingly unique feature in the fact that it yields only a single melting
endotherm, which is the P-III peak (or merged P-I and P-III). The ‘edge-on’ lamella in sPS indicates a very thickened (and branched) lamella, and the edge-on lamellae, grown at 260°C or higher, are no longer those within a regular spherulite. They are actually more similar to ‘axialites’ found in Regime-I growth. Bassett and Vaughan [56] also discussed interesting lamellar morphology of melt-crystallized iPS (isotactic), and suggested that polymer spherulites can form independent of the mechanism of Keith and Padden [57–59], in which axialites in iPS (when melt-crystallized at 220°C) were reported to exist.

4. Crystal forms in solvent-treated sPS

As mentioned earlier, the γ- and δ-forms are not usually seen in melt-processed sPS and commonly associated with solvent-induced crystallization in sPS [19]. More recently, details of various modifications in the δ-form crystal have been investigated [5,60–62]. This review is primarily concerned with the more common α- and β-forms in sPS, but for comparisons, the less common crystal forms (solvent-induced γ- and δ-forms) in sPS are briefly discussed. The δ-form is a monoclinic unit cell, and the chain conformation is helical. The γ-form can only be obtained by heating a δ-form to higher temperatures. The γ-form is also of a helical conformation, but the details of the γ-form crystallography and models have yet to be investigated and thus are not discussed here.
A proposed model for the crystal structure of the solvent-induced δ-form of sPS swelled by toluene molecules in the space \( P2_1/a \) is as follows \([60,61]\).\(^3\)

Dimensions: \( a = 17.58 \text{ Å}, \quad b = 13.26 \text{ Å}, \quad c (\text{chain axis}) = 7.71 \text{ Å}, \) monoclinic angle \( \gamma = 121.2^\circ \).
Different solvents produce a similar δ-crystal form in sPS. Solvent-induced clathrate δ-form of sPS swelled by dichloroethane (DCE) molecules in the space \( P2_1/a \) \([62]\).\(^4\)

\(^3\) The approximate \( z \) fractional coordinates of the barycenters of the phenyl rings are also shown. The carbon atoms which give the lowest intermolecular contact distances between and inside \( ac \) layers of macromolecules are labeled with letters \( \text{A–H} \).

\(^4\) The atoms of the asymmetric unit (atoms 1–18) are labeled. The approximate \( z \) fractional coordinates of the barycenters of the phenyl rings are also shown. \( R = \text{right, L = left-handed chain} \). The letters \( \text{A–D, A', and B',} \) indicate the phenyl rings with the surrounding DCE molecules.
Crystal dimensions: $a = 17.11 \, \text{Å}, b = 12.17 \, \text{Å}, c = 7.70 \, \text{Å}$, and monoclinic angle $\gamma = 120^\circ$.

When solvents are driven off completely from the solvent-induced crystal, the packing remains the same, but the dimensions change slightly. A model for the crystal structure of the emptied $\delta$-form ($\delta$-form) of sPS in the space $P2_1/a$ is as follows [61]. This $\delta$-form differs from the previous ones in the crystal dimensions. The $\delta$-form has a reduced b-dimension in the unit cell.\(^5\)

Crystal dimensions: $a = 17.4 \, \text{Å}, b = 11.85 \, \text{Å}, c = 7.70 \, \text{Å}$, monoclinic angle $\gamma = 117^\circ$.

5. Conclusion

The various crystal forms ($\alpha$, $\beta$, $\gamma$, and $\delta$) in sPS and their related melting behavior, morphology, stability, thermodynamics, and kinetics, etc., are discussed in this review. Melt crystallization in sPS leads to coexisting $\alpha$- and $\beta$-crystals of various fractions, in contrast with solvent-treated sPS that produces $\delta$- and $\gamma$-crystals. The $\alpha$-crystal is a hexagonal unit cell, and the $\beta$-form, an orthorhombic unit cell. The $\alpha$-crystal is invariably produced as the major crystal species when sPS is cold-crystallized, whether as miscible blends or neat sPS. Higher maximum temperatures (soaking temperature at molten state) and longer residence times held in the melt favor the $\beta'$-type crystal formation. Four melting peaks are seen in a melt-crystallized sPS that contains both $\alpha$- and $\beta$-crystals. A series of careful analyses has been able to resolve the multiple melting in relationship with the various crystal types. P-I and P-III peaks are associated with melting of the $\beta$- ($\beta'$-) crystal while P-II and -IV are with melting of the $\alpha$-(($\alpha''$-) crystal in sPS. Usually, a semicrystalline polymer exhibits an annealing peak (a minor endotherm

\(^5\) The carbon atoms of the asymmetric unit are labeled with the numbers 1-16. The carbon atoms which give the lowest intermolecular contact distances between and inside ac layers of macromolecules are labeled with letters A-D, H-M.
just above the annealing temperature) associated with an isothermal annealing imposed. Interestingly, however, two minor endothermic peaks (P_{a,α} and P_{a,β} with the latter at slightly higher temperature) are found for each annealing imposed on sPS, and apparently it is an indication of melt-processed sPS containing co-existing two crystal types: the α'- and β'-crystals.

More recent studies have investigated the individual crystals in sPS by isolating them in sample preparation. Although melt-processed sPS normally contains various fractions of co-existing α- or β-crystal, sPS could indeed be prepared so that they contained only individually isolated α- or β-crystal. The α- or β-crystal can be individually characterized, and they exhibit quite different thermodynamic and kinetic characteristics. The α-crystal has a lower melting temperature than the β-crystal, with \( T_{m,α} = 281.7°C \) and \( T_{m,β} = 288.7°C \). The heats of fusion measured at the respective maximum crystallinity are also different between these two crystals: \( ΔH_{f,α} = 27.9 \text{ J/g} \) for the α-crystal and \( ΔH_{f,β} = 31.5 \text{ J/g} \) for the β-crystal, respectively. The crystallization kinetics of β'-crystal is a homogeneous nucleation with lower rates. By comparison, crystallization kinetics of the α-crystal is a heterogeneous nucleation with higher rates. Lamellar morphology and spherulites of α- and β-crystal also differ significantly; the spherulitic and lamellar morphology of the α-crystal suggests a highly nucleated mechanisms (normally seen in cold crystallization) while the β-crystal is a homogeneous nucleation with larger spherulites (as seen from melt crystallization). Thermodynamics/kinetics of the various crystals reflect a different stability in these crystals. The β'-type is more thermodynamically stable than the α'-type; therefore, when crystallized at higher temperatures, β'-crystal is the major species. But the α'-type is kinetically more favorable, which grows in faster rates when crystallized at lower temperatures. This review only briefly discusses the δ- and γ-crystal, which, owing to instability, have not been characterized in depth except for the series of thorough crystal analysis performed at ambient temperatures by De Rosa et al. The δ- and γ-crystal in solvent-treated sPS are more like mesophases (monoclinic cell packing with helical chain conformation) that transform readily to α- , β''- or β'-crystal upon heating the solvent-treated sPS to high temperatures near the melting.

Lower molecular weights and syndiotacticity in sPS leads to significantly higher fractions of β-crystal over the α-crystal when sPS is melt-crystallized. In addition, miscibility effect on the crystal forms, polymorphism, and melting behavior in sPS in comparison with the miscible blends involving sPS is also discussed. Two miscible polymer mixtures involving sPS are demonstrated as sPS/aPS and miscible sPS/PPO. The equilibrium temperature of sPS in the miscible polymer systems is lowered, leading to more complete melting of the α'-crystal in sPS/aPS or sPS/PPO in comparison to the neat sPS when held at the same \( T_{max} \). Miscible blends containing sPS have been found to favor growth of β-crystal when subjected to the same melt crystallization conditions. This can be fully explained using a stability/metastability chart of free energy vs. temperature for comparing the relative stability of α-crystal vs. β-crystal.

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