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Crystal forms in cold-crystallized syndiotactic polystyrene

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Abstract

Unique thermal treatments were performed and differential scanning calorimetry (DSC) and X-ray diffraction analysis were used to characterize the dominating crystal form(s) being developed in cold-crystallized syndiotactic polystyrene (s-PS) in comparison with melt-crystallized polystyrene. The DSC results revealed that there are three (or fewer depending on the temperature of melt-crystallization) sharp melting peaks (Peak-1, -2, and -3) for the melt-crystallized s-PS samples, but only one peak (broad-based) for the cold-crystallized s-PS (when scanned at 10°C/min). The X-ray result suggested that cold-crystallization at higher than 200°C (200 ~ 250°C) produced only α-type crystal (or majority). This is in distinct contrast with melt-crystallization, which produced a combination of α-type (Peak-2 and Peak-3) and β-type (Peak-1) crystals at lower temperatures (240°C or lower), or majority of β-type if at temperatures higher than 260°C. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Cold crystallization; Syndiotactic polystyrene (s-PS); Crystal form

1. Introduction

Since its successful commercial synthesis via stereospecific polymerization [1–3], syndiotactic polystyrene (s-PS) has been widely studied. Most semicrystalline polymers possess only one type of unit crystal cell; for others, polymorphisms are known to exist. Interestingly, s-PS may possess various combinations of four different crystalline unit cell forms (α, β, γ, δ) depending on thermal history and/or solution treatments [4–6]. Normally, α and β forms are obtained with melt-processed s-PS. 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 with a helical conformation. For melt-processed s-PS, combination of both α and β forms is obtained, but formation of the β form is proposed to be favored over the α-form in s-PS compression-molded under pressure [7]. The β form is also favored if s-PS is prepared by solvent casting at high temperatures [8], as well as from melt with particular control of temperature and time of crystallization. Guerra et al. [4] and De Rosa et al. [5] also found that crystallization of s-PS from melt produces different fractions of α and β forms depending on cooling rate. In addition, recent studies pointed out that melt-crystallization at high temperatures preferentially favors the formation of β-form [9,10]. Evans et al. [11] studied on thru-thickness variation of structure and morphology in injection-molded s-PS, and they found that relative fractions of α- and β-type crystals were different between the skin and center regions, indicating that difference in thermal histories led to variation of relative proportions of these two crystal types.

Upon melt-crystallization at several isothermal temperatures between 230 and 250°C, the relative fraction of the two types of crystals can change. The β-form crystal increases over α-crystal entity for the s-PS samples crystallized/annealed at higher temperatures closer to T_m. The X-ray diffraction evidence also shows that relative fractions of the α versus β forms are different for the s-PS samples melt-crystallized at different temperatures, with higher temperatures (closer to T_m) favoring formation of β-form crystal [10]. Moreover, it was proposed that individual crystal forms may be related to the multiple melting peaks in melt-crystallized s-PS. In addition, some higher-temperature melting endotherms may be associated with re-melting of re-crystallized entities of melted crystals. Multiple melting phenomenon in s-PS is thus quite complex.

Crystal forms in cold-crystallized s-PS were less studied and possible differences between cold- and melt-crystallized s-PS have not been reported in literature. Although cold-crystallization phenomenon is not commonly encountered in typical melt-processing of engineering thermoplastics, it would be interesting to investigate differences between

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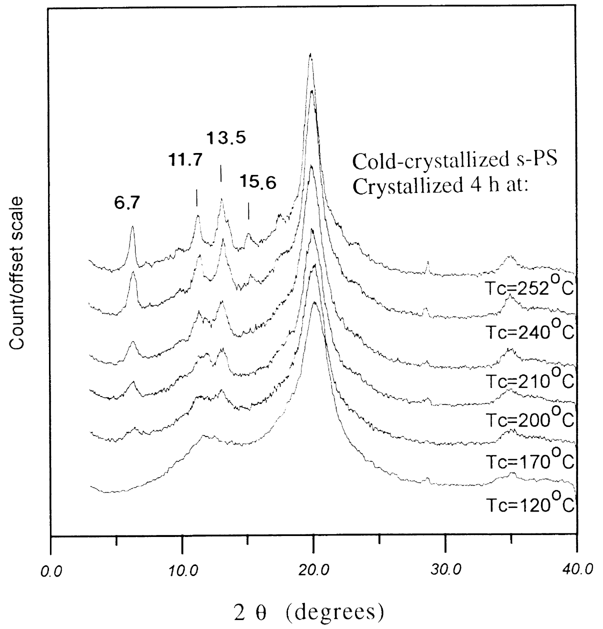

Fig. 1. X-ray diffractograms of s-PS samples cold-crystallized at several isothermal temperatures: 120, 170, 200, 210, 240 and 252°C for 240 min.

cold-crystallized and melt-crystallized s-PS, which constituted the objective of this study. s-PS samples of specific thermal histories were prepared by imposing delicately designed thermal treatment on s-PS samples, and thermal analysis and X-ray diffraction were performed on these samples to investigate characteristics of crystals and their melting behavior in cold-crystallized syndiotactic polystyrene.

2. Experimental

2.1. Materials and procedures

Semicrystalline syndiotactic polystyrene (s-PS) was obtained as a courtesy sample material from Idemitsu Petrochemical Co., Ltd. (Japan) with $M_w = 241{,}000$ g/mol and PI (M_w/M_n) = 2.31. For cold crystallization, initially amorphous s-PS was used. Amorphous s-PS (free of initial crystallinity) as a starting material was prepared by heating the as-received s-PS pellets to 310°C, compression-molded into a thin film (between two aluminum plate molds), then quenched quickly into liquid nitrogen or ice water. Transparent, crystal-free amorphous s-PS material was obtained upon quenching. The amorphous s-PS film was then cut into discs of proper sizes for various thermal treatments (cold-crystallization at designated temperatures for various times). Thermal treatments on samples were performed by placing the samples directly in a differential scanning calorimeter. After going through designated thermal treatments, they were ready for either DSC scanning experiments or X-ray diffraction characterizations.

2.2. Apparatus

The X-ray instrument used was Rigaku D/Max II-B with copper K_α radiation and a wavelength of 1.542 Å. For direct comparison, specimens of X-ray characterization were prepared using the similar thermal treatments as described for the thermal analysis samples. Differential scanning calorimetry (DSC-7, Perkin-Elmer) equipped with a mechanical intracooler was used for determining the melting transition temperatures and enthalpy of melting peaks. The temperature and heat of transition of the instrument were calibrated with indium and zinc standards at 10°C/min. A uniform heating rate of 10°C/min was used in all T_m measurements unless otherwise specified. If different scanning rates (lower or greater than 10°C/min) were used for special purposes, they were specified in texts or graphs. For exact temperature accuracy, all thermal treatments imposed on originally amorphous s-PS were performed in the cells of the differential scanning calorimeter. During thermal annealing or scanning, a continuous nitrogen flow in the DSC sample cell was maintained to ensure minimal sample degradation.

3. Results and discussion

3.1. Identification of crystal forms

X-ray diffraction was performed on cold-crystallized s-PS samples, which were compared to those for the s-PS melt-crystallized at equivalent isothermal temperatures, respectively. Fig. 1 shows the X-ray diffractograms for originally amorphous s-PS samples cold-crystallized at 120, 170, 200, 240 and 254°C, respectively for 240 min. The samples cold-crystallized at low temperatures (i.e. 120–170°C) contained little crystallinity and did not show discernible diffraction peaks, but all the s-PS samples cold-crystallized at 210, 240, or 252°C exhibited gradually sharper diffraction peaks at $2\theta =$ 6.7, 11.7, 13.2, 15.6, and 17.8°, which are typical of α'' form according to Guerra et al. [12]. Among the five peaks that increased, the three peaks at $2\theta = 6.7$, 11.7, and 17.8° are assigned to the β''-crystal according to De Rosa et al. [5]. Surprisingly, most characteristic peaks of the β'-crystal form (β', $2\theta = 6.1$, 10.4, 12.3, 13.6, 18.6, 20.2, 21.4, 23.9, 24.9, and 35°) are all absent from the cold-crystallized s-PS. The peak at 20.2° is characteristic of α and β forms and is present regardless of thermal treatment. The X-ray result indicates that the α-form crystal (hexagonal unit cell) dominates the crystalline domain of cold-crystallized s-PS.

It has been known [4,5] that s-PS samples melt-crystallized at higher temperatures (e.g. 254°C) exhibit diminished diffraction peaks of $2\theta = 6.68$, 11.58, 14.0, and 15.5°, which are characteristics of α-crystal. In addition, there exist two major types of crystal, α and β forms, in most melt-processed s-PS [3–5]. In general, although both α and β

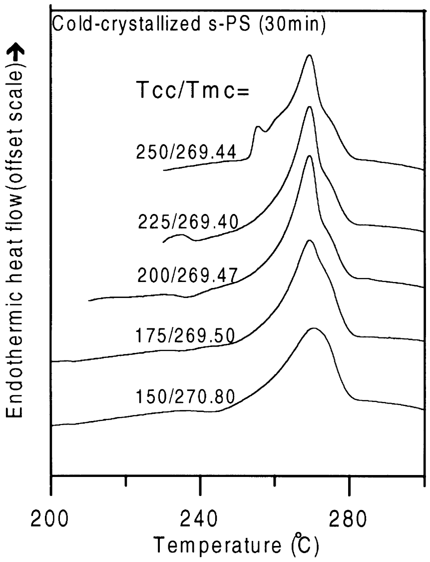

Fig. 2. DSC thermograms (10°C/min) of the s-PS samples that were cold-crystallized at 150, 175, 200, 225 and 250°C, respectively, for 30 min.

crystals could be found in melt-crystallized s-PS, the relative fraction of α- vs β-crystals are different depending on the temperature of crystallization and/or annealing. The result suggests that crystallization at relatively higher temperatures favors formation of β-crystal (orthorhombic unit cell), and lower temperature crystallization favors formation of α-crystal. But melt-crystallization always leads to samples containing different fractions of both types of crystals.

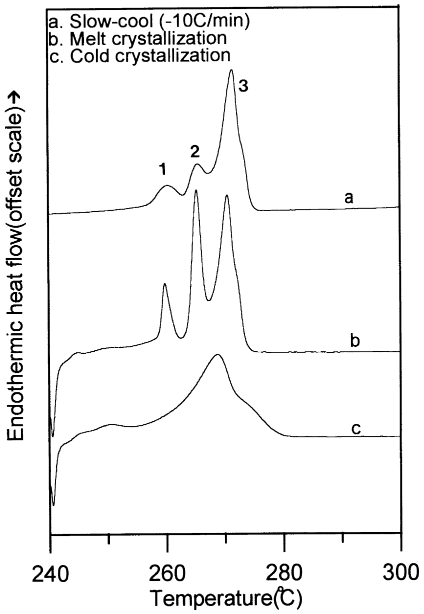

Fig. 3. Comparison of melting peaks of s-PS samples: (a) slow-cooled (−10°C/min), (b) melt-crystallized (240°C, 30 min) and (c) cold-crystallized (240°C, 30 min).

3.2. Melting peaks of cold- vs. melt-crystallized s-PS

Evidence of thermal transitions in cold-crystallized s-PS was examined. Fig. 2 shows the DSC thermograms (Curves a-e, all at 10°C/min) revealing an endothermic melting peak for the s-PS sample cold-crystallized at one of several isothermal temperatures: 150, 175, 200, 225, and 250°C, respectively, all for 30 min at each of the isothermal temperatures. Apparently, the thermograms exhibited a continuous trend of variation.If cold-crystallized at relatively low temperatures (e.g. 150°C or lower), the s-PS samples upon DSC scanning exhibited a round-shaped melting peak (with the peak at about 271°C). This melting endotherm has a similar peak temperature and similar roundness for all s-PS cold-crystallized at low temperatures ($T_{c,c}$ = 140, 150, 160°C). Apparently, cold crystallization at low temperatures led to incomplete crystallinity in s-PS and post cold-crystallization thermal history during DSC heating scans might help develop more perfected crystals, which upon scanning melted and yielded a similar melting peak for low temperature cold-crystallized s-PS. However, for cold-crystallization at gradually higher temperatures (e.g. 200°C and up), the samples upon scanning at the same rate displayed a slightly different melting peak. The melting peak is no longer round-shaped, but becomes sharper and appears to be composed of two partially overlapped peaks: a relatively sharp peak at 269.5°C. Interestingly, this peak temperature (269.5°C) remains at the same position regardless of the temperature of cold crystallization.

A direct comparison might help in explaining the melting behavior of the s-PS samples that are cold- or melt-crystallized. Two s-PS samples were prepared for DSC analysis, with one melt-crystallized at 240°C for 30 min and the other cold-crystallized at the same temperature of 240°C for the same time of 30 min. A third s-PS sample (labeled as ''slow-cooled'') was prepared by cooling s-PS at a constant slow rate (−10°C/min) from 300 to 50°C. These three s-PS samples were then scanned, respectively, in DSC all at 10 °C/min to generate their melting endotherm curves. Fig. 3 displays the DSC traces (a, b, & c) showing the melting peaks for three s-PS samples: (a) slow-cooled (−10°C/min), and (b) melt-crystallized, and (c) cold-crystallized at 240°C, 30 min, respectively. Both the slow-cooled s-PS and melt-crystallized s-PS exhibited similar features of three melting endotherms (T_1 = 260°C, T_2 = 265°C, T_3 = 272°C for Peak-1, -2, and -3). Peak-1 and Peak-2 for the slow-cooled s-PS (Thermogram-a) are much smaller in intensities than those for the melt-crystallized s-PS (Thermogram-b). However, there is apparently dramatic difference between the melt-crystallized s-PS samples and the cold-crystallized s-PS (Thermogram-c). 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 = 270.5°C, labeled as Peak-1, -2, and -3, respectively. Note that in addition to these three peaks, a high-temperature shoulder peak is also barely visible next to Peak-3. This

Table 1
Heat of fusion (measured at 10°C/min) for s-PS having subjected to cold- or melt-crystallization at isothermal temperatures for various times

Crys. Temp. (°C)	Time (min)	ΔH_f (J/g)
Cold-crystallized s-PS		
150	30	29.8
175	30	28.6
200	30	29.5
225	30	29.3
240	30	28.3
250	30	31.2
250	240	32.6
Melt-crystallized s-PS		
240	30	24.2
250	30	28.1
250	240	28.3
Slow-cooled ($\Delta H_c = 26.7$ J/g)		
		26.6

shoulder peak is labeled as Peak-4, which would become evident as a separate peak if the sample was scanned at a slower rate (e.g. 5°C/min). By comparison, the cold-crystallized sample displayed a single merged peak (269°C), regardless the temperature at which cold-crystallization took place. The single peak (but broad-based) for the cold-crystallized sample is likely merged signal of several melting peaks. At the slightly higher temperature, a shoulder is also seen with a barely-visible magnitude, or almost negligible, in comparison to the major sharp peak at 269.5°C. By judging from the temperature locations, it may be regarded as a combined thermal signal of Peak-3 and Peak-4 (shoulder peak), with probably small amount of under-developed crystal of Peak-2. Extending the time of cold crystallization led to only minimal changes. If the time was extended from 30 to 240 min but the temperature of crystallization was kept at the same temperature of 240°C, the s-PS samples upon DSC scanning exhibited similar-pattern melting peaks, with only slightly enhanced intensity with increasing time but minimal change in the peak temperatures (Table 1).

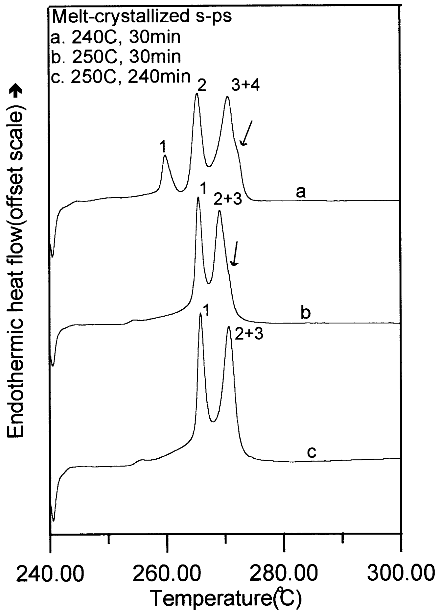

Fig. 4. Effects of temperature and time of crystallization on melting endotherms of s-PS samples: (a) melt-crystallized ($T_{m,c}$ = 240°C, 30 min), (b) melt-crystallized ($T_{m,c}$ = 250°C, 30 min), (c) melt-crystallized ($T_{m,c}$ = 250°C, 240 min).

Effects of higher temperatures (higher than 240°C) and/or more extended time (longer than 30 min) of melt crystallization were investigated by comparing the s-PS samples subjected to melt crystallization at two different temperatures or times. Fig. 4 (a,b,c) shows the DSC traces of melting peaks of s-PS samples melt-crystallized, respectively, at (a) 240°C for 30 min, (b) 250°C for 30 min, and (c)250°C for 4 h. The melt-crystallized sample upon scanning (at 10°C/min) exhibited three or two distinctly sharp peaks depending on the temperature of melt crystallization. As discussed earlier for melt crystallization at 240°C (for 30 min), three sharp peaks (not including a high-temperature shoulder peak) are clearly present. Note that adjacent to Peak-3 is a shoulder peak, which actually is a separate peak that could have been more evident if the same sample (240°C-melt-crystallized) were scanned at rates lower than 10°C/min (e.g. 2.5°C/min or 5°C/min). Thus, this shoulder peak may be viewed as Peak-4. The origin of Peak-4 is beyond the scope of this short article and thus it is not discussed here, but will be addressed in forthcoming reports. Upon melt crystallization at 250°C, however, only two sharp peaks (and a shoulder peak) are evident, which are located at 266 and 270.7°C, respectively. These two peaks correspond to Peak-1 and -2, respectively, with Peak-3 diminishing to appear as a shoulder peak. A lower scanning rate (2.5°C/min) revealed that Peak-2 actually was a merged peak comprising Peak-2 and trace Peak-3 (greatly reduced but still visible). Effect of temperature of crystallization is quite obvious. Melt crystallization at different temperatures led to different number of melting peaks as well as different peak temperatures, indicating possible effects of temperature on crystal forms and/or lamellar thickness. Melt-crystallization at 250°C led to that the peak temperatures of Peak-1 (at 266°C) and Peak-2 (271°C) were significantly elevated (by 6°C) in comparison to those (Peak-1 = 260°C, Peak-2 = 265°C) of s-PS melt-crystallized at 240°C.

It has been earlier reported [10] that for the melt-crystallized s-PS sample, three peaks are clearly seen, which are labeled as Peak-1, -2, and 3, respectively. The assignment of melting peaks (Peaks 1, 2, and 3) to possible crystal forms follows the analyses in previous reports [10,13]. There was less disagreement in that Peak-1 is attributed to the β-crystal, while Peak-2 is related to the α-type. In general, the comparison of DSC traces a, b and c in Fig. 4 also shows that for melt-crystallized s-PS samples subjected to further annealing at higher temperatures, more fraction of originally existing α-type (Peak-2) may be transformed to β-type (Peak-1) but not vice versa. This was further evidenced by

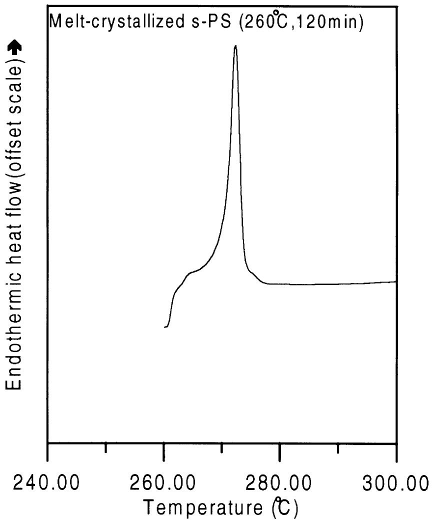

Fig. 5. DSC trace of the s-PS melt-crystallized at 260°C for 120 min., giving only an enhanced Peak-1 ($T_m = 272$°C).

DSC traces (not shown for brevity) that for the melt-crystallized s-PS samples annealed at a high temperature (between 240 and 260°C) for extended time, the intensities of Peak-3 and Peak-2 diminished (α-type), while the intensity of Peak-1 (β-type) increased.

However, the origins of Peak-3 and the shoulder Peak-4 are less understood. It has been reported [10] that upon extended isothermal holding at high temperatures (250 ~ 254 °C), the intensity of Peak-3 eventually diminishes and disappears. We further investigated the melting behavior of s-PS upon crystallization at even higher temperatures. Upon crystallization at an even higher temperature (e.g. 260°C) for 120 min., Peak-2 also disappeared, leaving only a greatly enhanced Peak-1 ($T_m = 272$°C). This is shown in Fig. 5. From these trends of peak shifting, Peak-2 and Peak-3 may be both associated with the α-form crystal. This is in agreement with the earlier reported X-ray result that the s-PS upon melt-crystallization at higher temperatures exhibits enhanced signal of β-crystal and diminished signal of α-crystal [10].

4. Conclusion

The X-ray result indicated that only α-type crystal existed in cold-crystallized s-PS, which yielded a single, but broad-based melting endotherm with the peak temperature remaining almost constant at 269°C regardless of temperature of cold crystallization (200 ~ 260°C). Thus, several probing questions regarding multiple melting peaks and crystal forms in cold-crystallized vs. melt-crystallized s-PS can be tentatively answered. Cold-crystallization at temperatures lower than 200°C led to only imperfect crystals (no distinct diffraction peaks) and cold-crystallization at higher than 200°C (200 ~ 260°C) produced only α-type crystal (or majority).

Cold crystallized s-PS differs significantly from melt-crystallized s-PS in crystal forms and melting behavior. Melt-crystallization at lower temperatures (240°C or lower) produced combination of α-type (Peak-2, and -3) and β-type (Peak-1) crystals. In general, the lower melt crystallization temperature favors the α-type while higher crystallization temperature tends to favor the β-type, leading to various fractions of α and β-types depending on the temperature of melt crystallization.

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References

[1] Ishihara N, Seimiya T, Kuramoto M, Uoi M. Eur Patent Appl, 210615 (1987).
[2] Pellecchia C, Longo P, Grassi A, Ammendola P, Zambelli A. Macromol Chem Rapid Commun 1987;8:277.
[3] Ishihara N, Seimiya T, Kuramoto M, Uoi M. Macromolecules 1986;19:2464.
[4] Guerra G, Vitagliano VM, De Rosa C, Petraccone V, Corradini P. Macromolecules 1990;23:1539.
[5] De Rosa C, Rapacciuolo M, Guerra G, Petraccone V, Corradini P. Macromolecules 1992;33:1423.
[6] De Rosa C. Macromolecules 1996;29:8460.
[7] Sun Z, Morgan RJ, Lewis DN. Polymer 1992;33:660.
[8] Chatani Y, Fuji Y, Shimane Y, Ijitsu T. Polym Prepr Jpn 1988;37:428.
[9] Vittoria V, Ruvolo Filho A, De Candia F. J Macromol Sci Phys 1992;B31:133.
[10] Woo EM, Wu FS. Macromol Chem Phys 1998;199:2041.
[11] Evans AM, Kellar EJC, Knowles J, Galiotis C, Carriere CJ, Andrews EH. Polym Engng Sci 1997;37:153.
[12] Guerra G, Vitagliano VM, De Rosa C, Petraccone V, Corradini P, Karasz FE. Polym Commun 1991;32:30.
[13] Hong BK, Jo WH, Lee SC, Kim J. Polymer 1998;39:1793.