ID 1007

Property-Structure Studies on Cold-Crystallized Syndiotactic Polystyrene and Its Composites

E. M. Woo and Ya Sen Sun

Department of Chemical Engineering, National Cheng Kung University, Tainan,

701-01, Taiwan，China

SUMMARY: Syndiotactic polystyrene (sPS) is a relatively new comer as an engineering semicrystalline polymer, which is often used in a composite form (glass-reinforced) for manufacturing electronic devices (connectors, switches, etc). Scanning electron microscopy (SEM), differential scanning calorimetry (DSC), infrared (IR) spectroscopy, and X-ray diffraction (XRD) analyses were used to characterize the structure-property relationships of cold-crystallized sPS. Cold-crystallization of sPS produced only the α-crystal unit cell packed into crystalline domains of different morphologies. The morphology contains a granular-sphere texture when cold-crystallized at low temperatures while high-temperature cold-crystallization produced additional sheaf-like lamella radiating out from the central spheres. Relationships between the morphology and melting behavior were investigated. Kinetics of crystallization and effects of blend miscibility on the crystal and morphology were also tentatively explored.

KEYWORDS: Cold crystallization, syndiotactic polystyrene (sPS), structure, property.

INTRODUCTION

Most semicrystalline polymers possess only one type of crystal unit cell, but some others may possess polymorphism with different chain-packing crystals. Interestingly, sPS may possess various combinations of four different unit cell forms (α, β, γ, δ) depending on thermal history and/or solution treatments.[1-4] Normally, co-existing α and β forms are obtained with 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 with a helical conformation,[5,6] In addition,

recent many studies point out that melt-crystallization at high temperatures preferentially favors the formation of the β-form.[7-9] Morphology in cold-crystallized sPS has been less studied. It has been preliminarily shown that cold-crystallized sPS differs significantly from melt-crystallized sPS in crystal forms and melting behavior.[10] This study aimed to understand in more detail the main characteristics of spherulitic or lamellar morphology and relationship between morphology, unit cell crystal forms, and thermal behavior in cold-crystallized sPS.

EXPERIMENTAL

Semicrystalline syndiotactic polystyrene (sPS) was obtained as a courtesy research sample material from Idemitsu Petrochemical Co., Ltd. (Japan) with a medium M_w = 63,000 g/mol and PI (M_w/M_n) = 2.8 (powder form). For cold crystallization, initially amorphous sPS was prepared as a starting material. Amorphous glassy sPS (free of initial crystallinity) as a starting material was prepared by heating the as-received sPS (powder) to 310^{o}C, compression-molded into a thin film, then quickly quenched into liquid nitrogen. For exact temperature accuracy, all thermal treatments of sPS samples for the X-ray SEM, or POM analyses were all performed in the cells of the differential scanning calorimeter.

RESULTS AND DISCUSSION

A preliminary study in this laboratory has revealed interesting morphology features in cold-crystallized sPS[11], which presumably contained only major fraction of α-crystal packed into an interesting morphology characterized by central granules with radiating lamellae. **Figure 1** (data from Ref.[11]) shows the POM & SEM morphology for the sPS samples of different thermal treatments: (Graphs A1&2) cold-crystallized at 150^{o}C, in comparison with (B1&2) cold-crystallized at 260^{o}C, all for 120 min. The optical graph (A1) shows tiny granular structures in sPS cold-crystallized at a low temperature of 150^{o}C. Graph A2 shows the morphology in sPS cold-crystallized at 150^{o}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. At low temperatures, cold-crystallization yielded a unique morphology of aggregation of many tiny underdeveloped spherulites, which may be due to lower molecular mobility during lower crystallization temperature. On the other hand, Graphs B-1&2 show that post-development of lamellar morphology surrounding the tiny spheres was observed if the sPS was cold-crystallized at increasingly higher temperatures. The POM graph

(B1) shows that when cold-crystallized at the highest temperatures (260^{o}C), only irregular lamellar structures were visible. SEM graph B2 shows that sPS cold-crystallized at 260^{o}C for 120min developed a peculiar morphology consisting of tiny crystals in the spherical center with secondary lamellae radiating out from the spheres. The thermal behavior, lamellar morphology, and correlation between melting and different lamellae in the cold-crystallized sPS containing only α-type unit cell were also investigated in details. The tiny granular spherulites, produced in low-temperature cold-crystallization, yielded a broad melting endotherm with the peak temperature remaining almost constant at 268~270^{o}C.[10] This melting behavior may be attributed to the roughly similar lamellae thickness distribution in the tiny spherulites regardless of temperature of cold crystallization. On the other hand, the radiating sheaf-like lamella (outside the spheres), produced in high-temperature cold crystallization, yielded a rather sharp melting peak.

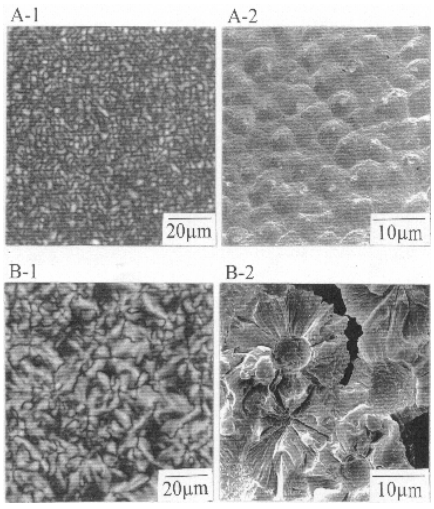

Figure 1. POM & SEM graphs for the sPS samples: (A1&2) cold-crystallized at 150^{o}C, (B1, B2) cold-crystallized at 60^{o}C, all for 120 min. (data from Ref.[11])

The thermal behavior, lamellar morphology, and correlation between melting and different lamellae in the cold-crystallized sPS containing only α-type unit cell were also investigated in details. The tiny granular spherulites, produced in low-temperature cold-crystallization, yielded a broad melting endotherm with the peak temperature remaining almost constant at 268~270^{o}C.[10] This melting behavior may be attributed to roughly similar lamellae thickness distribution in the tiny spherulites regardless of temperature of cold crystallization. On the other hand, the radiating sheaf-like lamella (outside the spheres), produced in high-temperature cold crystallization, yielded a rather sharp melting peak superimposed on the original broad melting peak. High-temperature cold-crystallization produced increasingly

higher fractions of the α-crystal (α”-modification) packed into the sheaf-like lamella. The melting of such lamellae of the α”-crystal yielded a rather sharp melting peak.

Melt-crystallization of sPS could also be conducted to produce only α-crystal under special conditions. SPS was first brought to a molten state by soaking at low T_{max} (280°C), which was then quenched to 240°C for 30 min to develop α-crystal (α’-

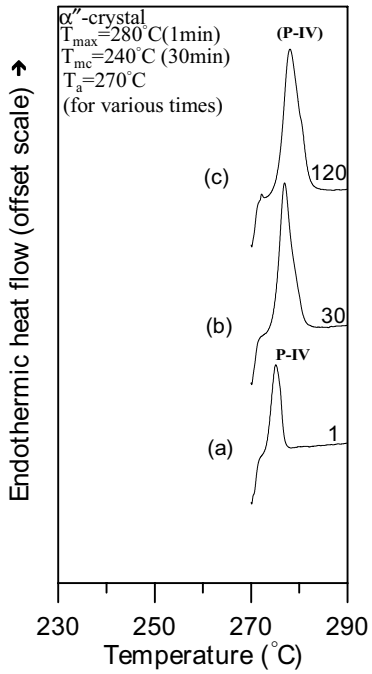

Figure 2. Melting behavior of the α”-crystal in sPS post-annealed at 270°C for different times: (a) 1 min, (b) 30 min, and (c) 120 min.

and α”-modifications). Upon post-annealing at 270°C, radiating sheaf-like lamella with the α”-crystal were formed. **Figure 2** shows the melting behavior of the α”-crystal in sPS post-annealed at 270°C for different times: (a) 1 min, (b) 30 min, and (c) 120 min. The DSC result apparently revealed an increasingly greater intensity of the melting peak (P-IV) attributed to the α”-crystal in the sPS annealed for longer times at 270°C.

Kinetics of crystallization

Cold-crystallization of sPS has been earlier tentatively investigated.[12] An Avrami exponent of nearly n=1.4 has been found for cold-crystallization of sPS. It has been suggested that cold-crystallization lead to predominantly α-crystal. Recently, appropriate techniques have been developed to prepare samples containing the individual crystals (α- vs. β-crystal) in sPS. It would be interesting to compare the cold crystallization to the melt crystallization of individual crystals (α- vs. β-crystal)

in sPS. Melt-crystallization kinetic analysis was performed on individually isolated crystal in sPS (α-crystal in comparison with β-crystal). The classic Avrami equation used for crystallization analysis is:[13]

$$1-X_t = \exp[-kt^n], \quad (1)$$

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

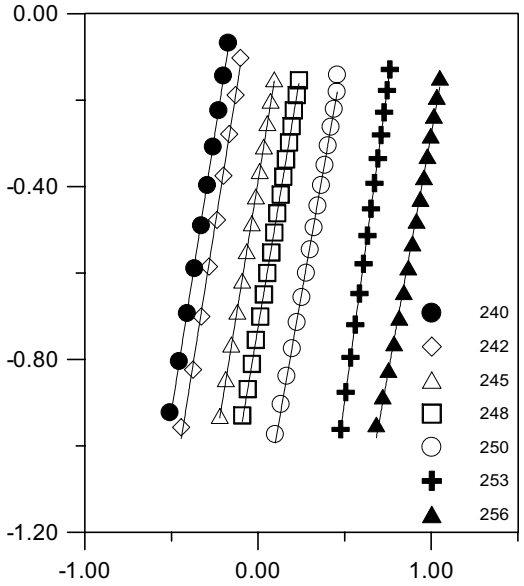

Figure 3. Melt crystallization of the α-crystal in sPS (data from Ref.[14]).

and growth geometry of the crystals. X_t 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, ΔH_c, in the DSC curves. That is, $X_t=\Delta H_c(t)/\Delta H_c$. Melt-crystallization kinetics of the α-crystal and β-crystal was respectively analyzed. The sPS sample could be prepared in such ways that it contained only α-crystal (α″-modification) by being crystallized at 240°C~256°C (pre-soaked at T_{max}=280°C for 1min at melt prior to being brought to crystallization). **Figure 3** (data from Ref.[14]) shows the plots for the melt crystallization of the α-crystal in sPS. The figure reveals that within a series of isothermal crystallization experiments, the Avrami exponent n is temperature-independent. If the average is taken as a representative value, the exponent was n = 1.5±0.1. The average value of n=1.5 for the α-crystal could be attributed to 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 melt crystallization of the α″-type is kinetically more accessible.

Figure 4 shows the X-ray crystallograph of sPS material that was prepared in such

ways that it contained only initial β-crystal (β”-modification) by casting from an sPS solution (*1,1,2,2*-tetrachloroethane at 130°C). This is comparable with the result reported by Guerra et al.,[2] who claimed β”-modification in sPS when precipitated from the dichloromethane/sPS solution.

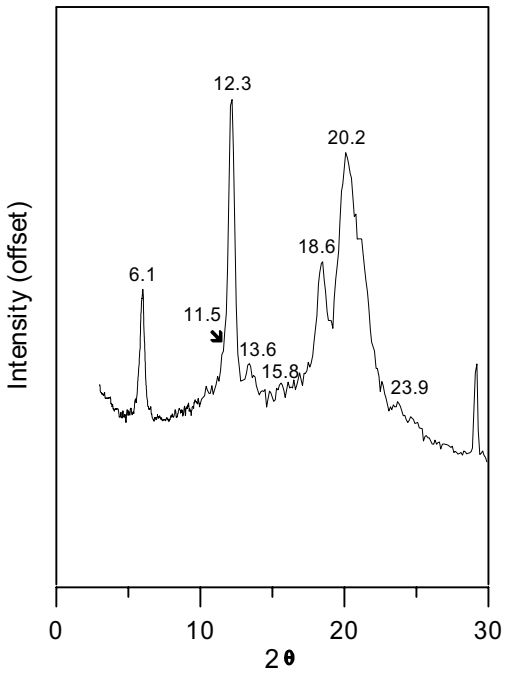

Figure 4. X-ray crystallograph of sPS material containing only initial β-crystal (β”-modification) by casting from sPS solution (*1,1,2,2*-tetrachloroethane at 130°C).

Crystallization kinetics of the β-crystal in sPS was similarly analyzed. As the solution-cast sPS (initially containing the β”-modification, as shownb in Fig. 4) was heated to the molten state at a high maximum temperature (T_{max}=380°C for 0.5 min) and quickly brought to melt crystallization, only the β’-crystal (no α-crystal) was found. The kinetics of melt crystallization of the β-crystal in sPS isothermally crystallized at 240°C~253°C (after pre-soaking at T_{max}=380°C for 0.5 min) were investigated for comparison. The average value of n was found to be 2.5±0.1 for the melt crystallization of the β’-crystal.

The kinetic parameters (n and k) for the individual α- or β-crystal were calculated. **Table 1** shows comparison of the kinetic parameters for melt crystallization of sPS leading to the individual α- or β-crystal, respectively. The value of n = 2.5~2.6 suggests that the crystal growth of the β-crystal is of a homogeneous nucleation and the growth pattern is 3-D spherical (with diffusion control). The growth rate of the α-crystal is faster than that of β, which is apparent by comparing the k values for these two crystals. More details of kinetic comparison are being investigated in a concurrent study and are to be summarized in a separate report.[14]

Table 1. Melt crystallization of α-crystal

T_c (°C)	n	k (min^{-n})
240	1.6	3.87
242	1.6	2.59
245	1.8	1.248
248	1.5	0.688
250	1.5	0.397
253	1.3	0.18

Initial form: quenched sPS; T_{max}=280°C (1 min),

Ave: n = 1.5±0.1 (α-crystal only)

Table 2. Melt crystallization of β-crystal

T_c (°C)	n	k (min^{-n})
240	2.6	2.3123
242	2.5	1.3805
245	2.5	0.4107
248	2.4	0.1886
250	2.3	0.0605
253	3.0	0.0043
256	2.2	0.0032

Initial form – solvent cast sPS; T_{max}=380°C (1 min)

Ave. n= 2.5±0.1 (β-crystal only).

The morphology of sPS containing the individual different crystal was examined and compared as well. The polarized optical microscopy (POM) result revealed tiny granular spheres in the melt-crystallized α-crystal (not shown for brevity), which is similar to that in the cold-crystallized sPS already shown in Fig. 1. The result further suggests that the α-crystal, regardless of cold- or melt-crystallization, is packed into a spherulitic morphology that may be different from the β-crystal. By contrast, large spherulites with significant impingement are the major morphology feature for the melt-crystallized β-crystal in sPS, which is distinctly different from the melt-crystallized α-crystal. The optical evidence for the α-crystal vs. β-crystal further supported that the β-crystal crystallized kinetics proceeded with a homogeneous nucleation mechanism, leading to fewer nuclei, slower rates, but much larger spherulites.

Miscibility effects

Miscible blends of sPS (with other polymers) are known to favor the β-crystal when melt-crystallized at most accessible temperatures, which is distinctly different from the neat sPS that upon melt crystallization develops mixed fractions of both α and

β-crystals. Cold crystallization of miscible blends of sPS/aPS in comparison with the neat sPS was also studied. The X-ray crystallograms of the sPS/aPS blend system cold-crystallized at a range of temperatures (150-260^{o}C) were inspected (for brevity, not shown). Interestingly, when miscible blends of sPS/aPS were cold-crystallized at low temperatures, only the α-crystal (with two modifications α' and α") was seen in the blend. However, at higher cold-crystallization temperatures (250 or 260^{o}C), the β-crystal along with the α-crystal was seen in the sPS/aPS blend system, which became more evident as the amorphous aPS content increased in the sPS/aPS blend. This is different from what has been observed in cold crystallization of neat sPS, which develops only the α-crystal regardless of temperature.[11] Thermal analysis on the cold-crystallized sPS/aPS blends could provide additional evidence of relative crystal stability comparison of the α–crystal vs. β-crystals. DSC characterization was performed on the sPS/aPS blend (75/25) samples cold-crystallized at 150, 175, 200, 225, 250, and 260°C, respectively. In all, the DSC results showed good agreement with the X-ray evidence. A broad melting endotherm (labeled as $P_{\alpha'}$), attributed to the α′-crystal, is seen in the samples cold-crystallized at low temperatures (150, 175°C), which is similar to those observed in cold-crystallized neat sPS.[10,11] In comparison, the melting and thermal characteristics of cold-crystallized sPS/aPS samples of higher amorphous aPS contents are distinctly different from those of neat sPS. This study is still in progress and more can be reported in the conference.

CONCLUSION

Cold-crystallization of sPS produced only the α-crystal (α'and α"-modifications) packed into the crystalline domains. The morphology of the crystalline domains is characterized with a granular-sphere texture when cold-crystallized at low temperatures (α') while high-temperature cold-crystallization produced additional sheaf-like lamella radiating out from the central spheres (α"). Relationships between the morphology and melting behavior were investigated. The kinetics of cold-crystallization of sPS were tentatively compared to those of the melt crystallization of the α-crystal in sPS and were found to be similar but were significantly different from the melt crystallization of the β-crystal in sPS. Effects of blend miscibility on the crystal and morphology in cold-crystallized sPS and its blend were explored in this study.

ACKNOWLEDGMENT

The work was supported by research grants from National Science Council (#NSC89 2216 E006 014 and others).

REFERENCES

1 Tosaka M, Tsuji M, Cartier L, Lotz B, Kohjiya S, Ogawa T, Isoda S, Kobayashi T. *Polymer* **39**, 5273 (1998).

2 Guerra G, Vitagliano VM, De Rosa C, Petraccone V, Corradini P. *Macromolecules* **23**,1539 (1990).

3 De Rosa C, Rapacciuolo M, Guerra G, Petraccone V, Corradini P. *Polymer* **33**,1423 (1992).

4 De Rosa C. *Macromolecules* **29**, 8460 (1996).

5 Sun Z, Morgan RJ, Lewis DN. *Polymer* **33**, 660 (1992).

6 Chatani Y, Shimane Y, Ijitsu T, Yukinari T. *Polymer* **34**, 1625 (1993).

7 Vittoria V, Ruvolo Filho A, De Candia F. *J. Macromol Sci Phys* **B31**,133 (1992).

8 Woo, EM, Wu FS. *Macromol Chem Phys* **199**, 2041 (1998).

9 Evans AM, Kellar EJC, Knowles J, Galiotis C, Carriere CJ, Andrews EH. *Polym Eng Sci* **37**, 153 (1997).

10 Woo EM, Sun YS, Lee ML. *Polymer* **40**, 4425 (1999).

11 Sun YS, Woo EM. *Polymer* (communications) **42**, 2241 (2001).

12 Wu FS, Woo EM. *Polym. Eng. Sci.* **39**, 825 (1999).

13 Avrami, M. *J. Chem. Phys*. **9**, 177 (1941).

14 Sun YS, Woo EM. *Macromolecules* (communications), submitted (2001).