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New Observations on the Formation of “Row-Nucleated” Structures of Isotactic Polystyrene

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ABSTRACT: A unique 60 °C endothermic peak was found in the differential scanning calorimetry (DSC) measurement of freeze-dried isotactic polystyrene (i-PS) prepared from a 0.01 wt % benzene solution. While i-PS was melted before preparing a solution at a temperature beyond the equilibrium melting point, nothing could be observed around 60 °C. The endotherm can be attributed to the melting of microgel crystals. Morphology observation revealed that ribbonlike films of i-PS were formed when the solution was spread on a cold water surface. After isothermal crystallization of the films, “row-nucleated” crystals were grossly produced without any extensional deformation of molecular chains. It is suggested that microgel crystals may act as heterogeneous species to initiate the growth of “row-nucleated” crystals.

Introduction

It is well-known that orientation-induced crystallization can result in the so-called “row-nucleated” structure.[1−4] Shish kebab is formed on crystallization from solution under condition of elongational flow, which induces a somewhat extended conformation of macromolecules. The shish kebab contains a fibrous crystalline core, the shish, onto which epitaxial secondary overgrowth of lamellae, the kebabs, is initiated.[1] While the melt or rubber is subjected to a high elongational flow in combination with a high pressure or a high cooling rate, a similar crystal morphology is formed and is usually termed as “row-nucleated” structure.[2] The lamellae grown from adjacent fibrils are interlocked in such crystals, a fact which is considered to be important for mechanical properties of polymer materials. Nevertheless, it seems that deformation has to apply to macromolecular chains for the formation of either “row-nucleated” structure or shish kebab.

In this paper, however, we have reported some new observations on the formation of “row-nucleated” structure of isotactic polystyrene. We found that “row-nucleated” crystals can be produced massively without the help of elongation field. Instead, we propose that the microgel crystals of i-PS can act as heterogeneous sites for the growth of “row-nucleated” structure.

Experimental Section

Isotactic polystyrene (i-PS) was purchased from Scientific Polymer Products, Inc. It had an isotacticity above 90%. The number-average molar mass was estimated to be 5.8×10^5 by gel permeation chromatography (GPC) with the highest molar mass fraction $M = 4.0 \times 10^6$. Reagent-grade benzene was used with normal safety precaution after distillation. The as-received i-PS sample was first melted in a sealed aluminum cell at 242 or 246 °C for 3.5 min under nitrogen and then quenched into the liquid nitrogen. This procedure led to amorphous i-PS. The amorphous i-PS was then dissolved in boiling benzene with aid of agitation to make a solution of 0.01 wt %. The solution was then poured into a round-bottom flask while it rotated rapidly and was immersed in liquid nitrogen, so that the solution frozen in a fraction of a second. The frozen solvent was sublimated at −15 to −10 °C in an ice−salt bath under vacuum. To get rid of trace benzene possibly remained between segments, a silicon-oil diffusion pump was used to reach a fine vacuum and lasted to run for about 5 h. After total sublimation of the solvent, the remaining fluffy particles were collected at the bottom of the flask and stored at −18 °C until use.

Differential scanning calorimetry (DSC) measurements were run at a heating rate of 20 °C /min in a nitrogen atmosphere with a Dupont 910 system. Here, 3−4 mg of the freeze-dried samples was used in each run. The instrument was calibrated with an indium standard before use.

A circular Teflon trough filled with deionized water was used to spread the i-PS solution. The 0.01 wt % solution was carefully dropped with a microsyringe onto the water surface, one drop at a time. The resulting amorphous i-PS films, floating on the water surface, were transferred to copper grids covered with colloidion film and reinforced with evaporated carbon, followed by isothermal crystallization at 175 or 125 °C for 8 h.

The crystal morphology was observed with a Philips CM-12 transmission electron microscope (TEM). Selected-area electron diffraction was carried out with the Philips CM-12 TEM at an operation voltage of 120 kV. To avoid radiation damage, the specimens were directly viewed in a diffraction mode with a minimum brightness and beam intensity. When the specimens were illuminated by slowly moving the sample stage, reflections could be easily found and diffraction patterns were then recorded with a proper brightness and exposure time.

Results

Differential Scanning Calorimetry Measurement. DSC traces of the freeze-dried particles of i-PS prepared from 0.01 wt % solution are shown in Figure 1. Of special interest is a small 60 °C endothermic peak appearing in the DSC trace of the virgin sample (curve A) with an enthalpy value of about 1−2 J/g. In principle, such an endothermic peak could be linked to the melting of a certain regular microstructure. How-

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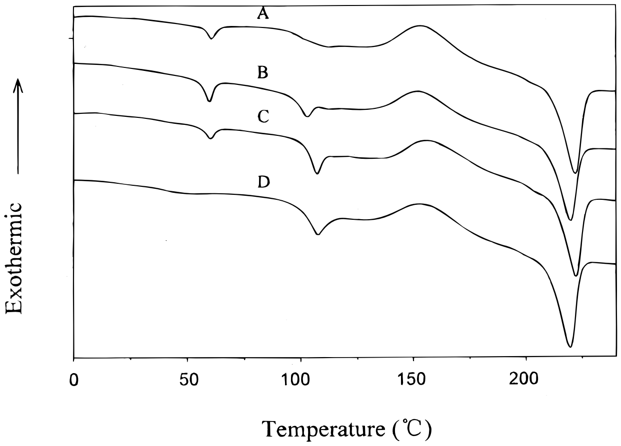

Figure 1. DSC traces of freeze-dried samples prepared from 0.01 wt % benzene solution containing self-nuclei: (A) virgin sample, (B) sample annealing at 80 °C for 1 h, (C) sample annealing at 80 °C for 10 h, and (D) sample annealing at 80 °C for 50 h.

ever, it was revealed in our previous papers that the freeze-dried i-PS is in a dilated and noncrystalline state.[5−7] Also, the 60 °C transition cannot be related to the glass transition temperature (T_g) of bulk i-PS, which is around 100 °C. More surprising is the fate of this structure upon annealing at 80 °C. When the annealing time is less than 10 h, the endothermic peak still remains, and the peak is only shifted to a slightly higher temperature. Only after 50 h of annealing does this peak finally disappear (curve D in Figure 1). This behavior is different from what happens on melting of chain-folded crystals where amorphous state is obtained with an instant change in the chain conformation from folding to random coil.

After annealing, there is another endothermic peak appearing around 100 °C in the DSC traces of those annealed samples. Such an endothermic peak originates from physical aging, which usually occurs in most of amorphous polymers upon sub-T_g annealing.[8] The enthalpy change caused by physical aging is also on the order of 1−2 J/g. Additionally, all freeze-dried samples show an exothermic peak around 150 °C either before or after annealing, which is attributed to cold crystallization. Melting of crystals produced by cold crystallization is around 220 °C (Figure 1).

Naturally, one may ask what is the mechanism responsible for the occurrence of the 60 °C endothermic peak. It was reported that the melting point of gel crystals of i-PS is between 50 and 120 °C. Then, is it proper to attribute the 60 °C small endothermic peak to the melting of gel crystals? According to the previous literature, the gelation of i-PS solution relies upon two criteria.[9−11] One is the requirement of quenching of hot solution to room temperature, and the other is the concentration criterion; i.e., a critical concentration has to be reached. It was suggested that the gelation of i-PS in the Decalin solution does not occur until the solution concentration is above 1.4%.[12] However, the freeze-dried samples of i-PS here were prepared from a dilute solution of 0.01wt %, far below the critical concentration of gelation. In fact, the concentration is even lower than the overlapping concentration C^*.[13] Therefore, most of the chains should exist in the form of single-chain coils in the solution. In principle, one cannot expect to produce gel crystals of i-PS from such a dilute solution.

Attention should be given to the details of preparation of this dilute solution. As the i-PS is a semicrystalline polymer with a rather high melting point and a large melting enthalpy, it is very difficult dissolve it in benzene, even though the benzene solution is heated. However, the amorphous i-PS can be easily obtained by quenching from the melt, and it is dissolved quickly in benzene even at room temperature. What we did first was to melt the as-received i-PS powder at a temperature beyond the equilibrium melting temperature (T_m^0) of i-PS (243 °C).[14,15] When the powder is melted at 242 °C or a lower temperature, the small 60 °C endothermic peak can always be observed. It was well-known that some small crystals with a high thickness or an extended-chain conformation can survive from melting when the melting temperature is lower than T_m^0, and they subsequently initiate crystallization during the cooling process and are termed as self-nuclei. Therefore, the i-PS melted at a temperature below T_m^0 cannot dissolve completely in hot benzene to form a homogeneous solution. Those remained crystal fragments or crystalline “cores”, however, were likely to be invaded by benzene molecules and thus would be swollen somewhat. Accordingly, local solution concentration in the swollen species would be higher than the critical value of gelation. This is why a small quantity of gel crystals can be produced from swollen “cores” during quenching and why the melting of gel crystals causes the small endothermic peak at 60 °C. During the annealing at 80 °C, microgel crystals may melt at the beginning, but the extended-chain conformation still remains and recrystallization occurs with improved perfection. Finally, the crystals were melted and the extended-chain conformation relaxed during long period of annealing, and thus the small peak at 60 °C disappeared.

As a parallel experiment, the bulk i-PS was melted at 246 °C, 3 °C above the T_m^0 of i-PS, to destroy all ordered structures. Therefore, no crystalline remnant was present, and the resulting i-PS/benzene solution was completely homogeneous. In this case, we could not find any additional endothermic peaks at 60 °C in the DSC traces of the freeze-dried samples.[6,7]

Morphology Observation. About 100 μL of a hot i-PS solution of 0.01 wt % containing self-nuclei was spread on a water surface of 30 cm^2. The spreading of the solution was very quick, and the benzene was rapidly evaporated off. After complete evaporation of the solvent within a short time, the amorphous i-PS films or particles were left on the water surface. They were then transferred to the copper grids, followed by isothermal crystallization at 175 °C for 8 h. Large quantities of ribbonlike “row-nucleated” structures were produced (Figures 2 and 3). It can be seen from Figure 2 that these ribbons are separated and that each of them consists of a central crystalline fibril core with an overgrowth of lamellae around the core. These lamellae are viewed edge-on, and they are parallel with each other. They almost have the same thickness (~10 nm), but the width varies greatly with different ribbons. Such crystal morphology of these ribbons is the so-called shish kebab. The “row-nucleated” structure is observed to be more densely stacked (Figure 3) when twice amount of solution (200 μL) was dropped on the water surface. The peripheral lamellae nucleating onto adjacent fibrils are interlocked and thus a great number of taut tie chains are present between adjacent lamellae.

Figure 2. Transmission electron micrograph of "shish kebabs" of i-PS prepared from 0.01 wt % solution containing self-nuclei, crystallized at 175 °C for 8 h. 100 μL of solution was added onto the water surface. The scale bar indicates 500 nm.

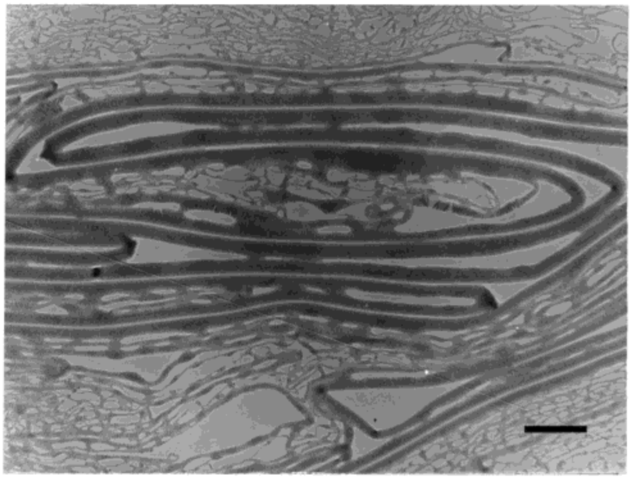

Figure 4. Transmission electron micrograph of shish kebabs of i-PS prepared from 0.01 wt % solution containing self-nuclei, crystallized at 215 °C for 8 h. 100 μL of solution was added onto the water surface. The scale bar indicates 500 nm.

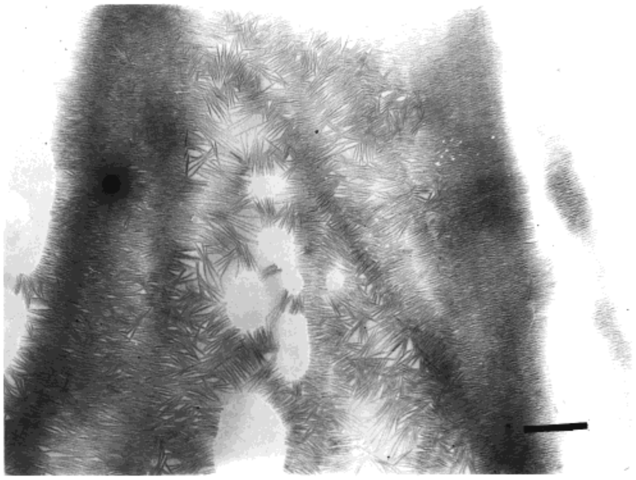

Figure 3. Transmission electron micrograph of "row-nucleated" structures of i-PS prepared from 0.01 wt % solution containing self-nuclei, crystallized at 175 °C for 8 h. 200 μL of solution was added onto the water surface. The scale bar indicates 500 nm.

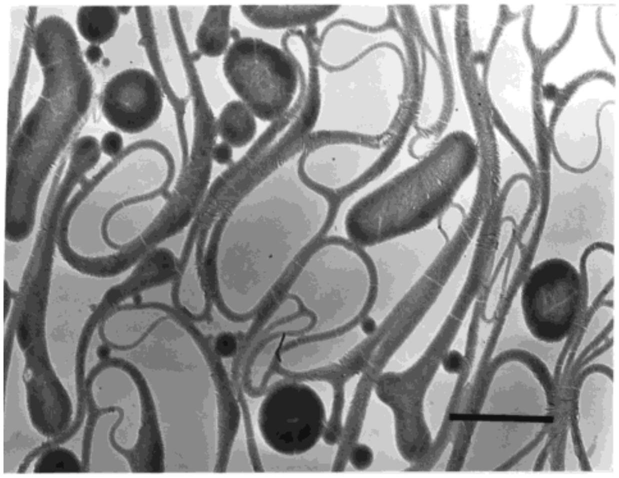

Figure 5. Transmission electron micrograph of ribbonlike crystals of i-PS prepared from 0.1 wt % homogeneous solution without self-nuclei, crystallized at 175 °C for 8 h. 20 μL of solution was added onto the water surface. The scale bar is 5 μm.

Figure 4 shows "row-nucleated" crystals grown at 215 °C for 8 h. Compared to the morphology in Figure 2, the lateral dimensions of lamellae are much shorter. The epitaxial grown lamellae might be melted partially at this temperature, and thus boundaries between adjacent lamellae become rather vague in contrast with the distinct separated lamellae in Figures 2 and 3. At the lower and upper parts of Figure 4, some delicate ribbons were observed. Nevertheless, most of them still have "row-nucleated" structures.

For the purpose of comparison, 20 μL of 0.1 wt % homogeneous solution of i-PS was used instead. The resulting beautiful ribbonlike crystals are shown in Figure 5. Close observation reveals that the ribbons are in fact aggregates of multilayer lamellae. Some lamellae lie flat on the substrate; others are placed edge-on. The lamellae lying flat on the substrate have the *c*-axis (chain axis) normal to the substrate. The classical theory of crystallization[16] suggests that the lamellae with such an orientation should be initiated by homogeneous nucleation, rather than heterogeneous nucleation on the carbon–film substrate. In some cases, spherulites and sheaflike structures were also developed. Evidently, the morphologies shown in Figures 2 and 5 are totally different in character. There should not be any elongational flow in the formation process of ribbons, or else "row-nucleated" structures should have formed in both cases. Therefore, the formation of "row-nucleated" structures can be related to the preexistence of microgel crystals, which were produced on quenching the solution containing self-nuclei onto the cold water surface.

Selected-Area Electron Diffraction. Figure 6a shows selected-area electron diffraction (ED) pattern of "row-nucleated" crystals. It is seen that as many as seven reflections are clearly observed. The ED pattern indicates a high-oriented structure in the sample. The crystalline i-PS has a trigonal unit with $a = b = 2.19$ nm and $c = 0.67$ nm and its space group is $R3C$.[17] The chains passing through the unit cell have 3_1 helix conformations. All observed reflections have been indexed (Table 1) according to the unit cell. However, none of the reflections corresponds to the gel crystal structure of i-PS. Upon isothermal crystallization at 175 °C, the gel crystals must have been melted and their characteristic reflections completely disappear. In Figure 6a, the (012) and (211) become the first and second stron-

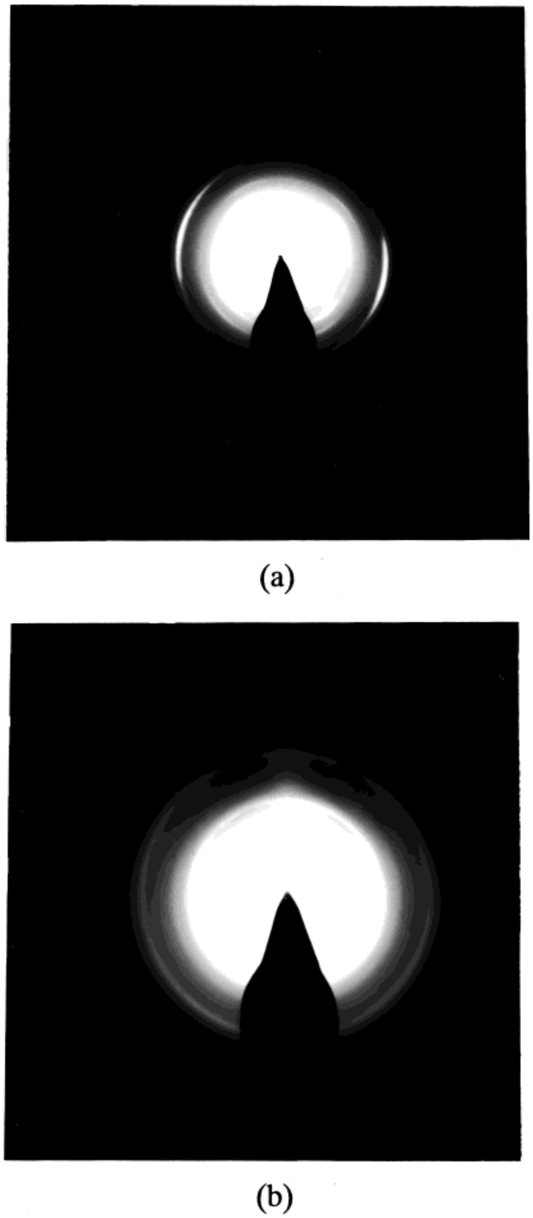

Figure 6. Selected-area electron diffraction pattern of “row-nucleated” crystals of i-PS: (a) grown at 175 °C; (b) grown at 215 °C.

gest reflections, respectively, and the (612) reflection arc is also rather bright. This situation is quite different from the common powder wide-angle X-ray diffraction pattern of i-PS, in which the (220), (110) reflections are the two strongest peaks. As is seen from Figure 6a, both of them turn out to be extremely weak. On the basis of the calculations of structure factors, we know that the [100] incidence pattern yields the strongest (012) reflection and the corresponding [010] incidence pattern yields the strongest (102) reflection. In the “row-nucleated” structures, the epitaxial grown lamellae are all placed edge-on. Therefore, it is hardly surprising to see that all the (*hk*0) reflections become rather weak and even disappear as the chain axis ([001] direction) is perpendicular to the incident electron beam. Moreover, the ribbons composed of “row-nucleated” crystals are closely packed and parallel with each other, leading to a similar orientation of lamellae grown from different ribbons and the formation of high-oriented ED pattern.

The ED pattern of row-nucleated structures grown at 215 °C is shown in Figure 6b. Only a few weak reflection rings are seen instead of the bright discontinuous arcs in Figure 6a. The (012) reflection still remains the strongest one. However, most of the reflections are too weak to be seen. It thus confirms that adjacent lamellae amalgamation due to partial melting destroys the high-oriented structures in the sample.

Table 1. Observed and Calculated Lattice Spacings, Lattice Plane and Diffraction intensity

d(obsd), Å	relative intensity[a]	Miller indices (*hkl*)	*d*(calcd), Å
6.39	w	(300)	6.32
5.46	vw	(220)	5.47
4.86	vs	(211)	4.88
4.05	s	(131)	4.13
3.39	vs	(012)	3.28
2.96	w	(122), (312)	2.82
2.26	s	(612)	2.11

[a] Key: vs, very strong; s, strong; w, weak; vw, very weak.

Discussion

It was verified that elongational flow field is necessary to extend molecular chains for the formation of “row-nucleated” structures.[3] However, “row-nucleated” structures of i-PS can also form just with the help of microgel crystals, as is seen in this paper. In this case, there is no any strain applying to macromolecular chains. It is the microgel crystals that act as heterogeneous sites to start the growth of “row-nucleated” crystals. Obviously, heterogeneous nucleation has great thermodynamic advantages over homogeneous one. Figures 2−4 show the “row-nucleated” structures initiated by microgels in the sample; instead, the aggregates of i-PS crystals were formed (Figure 5) in the absence of self-nuclei when the melting temperature was beyond T_m^0.

It was generally accepted that the helical conformation is thermodynamically stable for most substituted polyolefins. In the case of i-PS, the molecular chain often adopts *tg* conformation and thus forms a 3_1 helix in the crystalline state.[17] Furthermore, it was also revealed that i-PS chains are likely to adopt a near trans-conformation in the gel crystalline state, although this crystal structure has not been definitely determined thus far.[18,19] In fact, Flory carried out energy calculations for a separated i-PS chain in some detail.[20] His result showed that both *tg* (0°, 120°) and *tt* (−20°, 20°) conformation are accessible for i-PS due to the attractive interaction of neighboring phenyl groups. In both gel and shish crystals of i-PS, molecular chains are most likely to adopt near *tt* conformation and form extended-chain structure. Our speculation seems to be self-consistent at this point. This work has disclosed a close relation between the gel crystals and the formation of “row-nucleated” structures of i-PS. However, the explanation to the new findings is tentative and left open to discussion.

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