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Transmission Electron Microscopy Observations on Lamellar Melting of Cold-Crystallized Isotactic Polystyrene

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When polymers crystallize, they can adopt a spherulitic morphology, where the lamellae grow outward radially,[1,2] or a shish-kebab morphology, which results if the polymer chains are highly oriented.[3−5] More detailed studies of polymeric systems showed that there were two distinct types of lamellar crystals present in the spherulites. Dominant, or leading, lamellae could be characterized by a thicker appearance and were identified as growing first to provide a skeleton for the spherulites. Secondary, or in-filling, lamellae were seen as being rather thinner and having an ill-defined orientation within the spherulites. These secondary lamellae were taken to have grown behind the main growth front, after the dominant lamellae, and served to fill in the spaces between the primary, leading lamellae.[6] What is unclear from models of polymer crystallization is how growth progresses and how lamellae interact when they come into contact with each other.[7] Most recently, an atomic force microscopy (AFM) study has imaged these processes. Li and co-workers show that secondary lamellae, which give rise to the curvature in a spherulite, form through branching caused by secondary nuclei that originate from leftover chain segments trapped in the parent lamellae (cilia).[8,9] Upon impingement of two growing lamellae, crystalline growth does not necessarily halt. Specified to isotactic polystyrene (iPS), its lamellar crystallization from both the melt and the glass was reported by Edwards and Phillips using transmission electron microscopy (TEM),[10] in which they observed that no physical branching of the lamellae is involved, but instead a new lamella crystal is nucleated some distance (up to 40 nm) away from a growing lamella, especially at points of stress concentration or localized strain.

Recent developments in the AFM characterization of polymers involve measurements at different temperatures (i.e., the application of in-situ hot-stage AFM),[11−13] which make it possible to image the crystallization and melting processes of polymers in real time, as used in poly(ethylene oxide) and its blends,[14,15] poly(hydroxybutyrate),[16] polyethylene,[4,17] and other polymeric systems.[8,9,18] Despite these extensive studies on crystalline morphologies of polymers by AFM, to our knowledge few detailed and systematic morphological observations at lamellar level have so far been carried out on the melting process of semicrystalline polymers by TEM. In this report, we demonstrate the lamellar melting and reorganization processes of isothermally cold-crystallized iPS by a series of TEM observations. Here, iPS is selected as the studied system mainly based on the following considerations: (1) The characteristic slow crystallization rate of this polymer makes it an ideal subject for the investigation of melting behavior in polymers, due to the possibility of following the crystallization and melting processes. (2) It has higher stability to electron irradiation than most other polymers.[19]

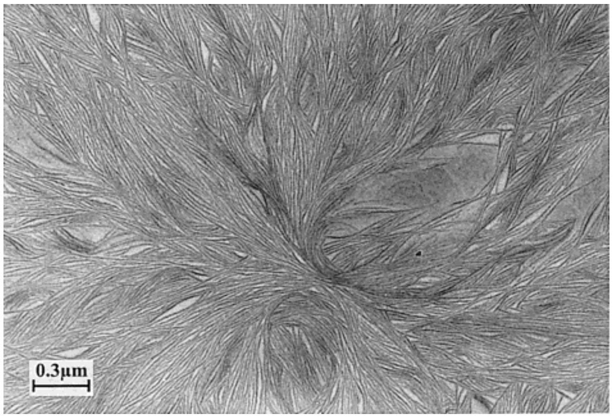

Figure 1. TEM bright field (BF) electron micrograph of an iPS thin film isothermally cold-crystallized at 160 °C for 6 h.

The powdery iPS sample ($M_w = 752\,000$, isotacticity 97%) was purchased from Polymer Laboratories. The glass transition temperature (T_g) and apparent melting point (T_m) were determined to be 98 and 220 °C, respectively, by differential scanning calorimetry (DSC-2920 from TA Instruments) at 10 °C/min. The equilibrium melting point was estimated as 242 °C.[20] Thin films for direct TEM observation were obtained by the following procedure. First, the dilute polymer−xylene solution (with concentration of 0.1% w/v) was dropped onto freshly cleaved mica covered with a carbon film. Then, the polymer films on the carbon−support film were floated onto the water surface and transferred onto electron microscope copper grids. After that, the obtained thin films on the grids were melted at 250 °C for 5 min in DSC and subsequently took out by rapidly quenching into ice water to get amorphous samples. Finally, the amorphous thin films were isothermally crystallized at 160 °C for 6 h. The obtained crystalline thin films were further partially melted or annealed at different temperatures for different times. All crystallization and melting treatments were performed in DSC under nitrogen atmosphere in order to diminish oxidation. Morphological observations were carried out using a Philips CM200 TEM operated at 200 kV, and the contrast in the bright-field (BF) electron micrographs of the thin films was obtained by defocusing the objective lens.[21]

Figure 1 shows the TEM BF micrograph of an iPS thin film cold-crystallized at 160 °C for 6 h. It can be seen that the well-developed spherulitic structure consisting of closely packed edge-on lamellae are the main characteristic morphology. A number of lamellar stacks continuously grow outward from the central regions by splaying and branching which usually result in the formation of both curved lamellae and “holes”, especially

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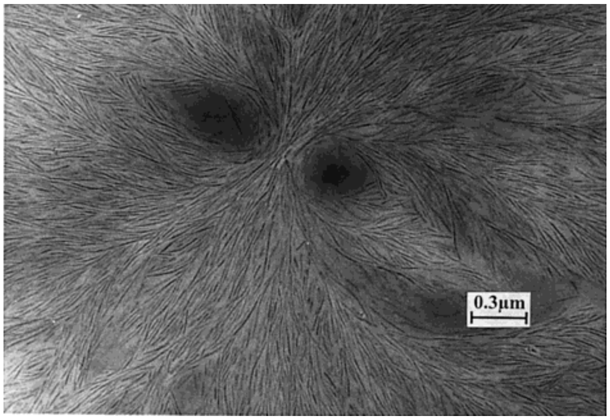

Figure 2. TEM BF electron micrograph of an iPS sample having the same thermal history as in Figure 1, which was further partially melted at 207 °C for 1 min and then rapidly quenched to room temperature.

in the outer regions of spherulite. The bending of a lamella is probably induced by the stress of the chain segments trapped among the lamellae.[9] In some places, growing lamellae encountered each other, thus restricting their further growth. Close inspection of the micrograph indicates that the shapes, sizes, and contrast of the individual lamellae vary over the spherulite, but little evident clarification into different categories of lamellae can be seen. However, we do not rule out the possibility of the existence of secondary crystals probably formed in between the framework of primary crystals due to the confined growth space (see below). Moreover, within one of the spherulitic "eyes", flat-on crystals can be observed.

To investigate the internal architecture of spheruiltes of iPS, partial melting experiments are performed. Typically, the originally crystallized samples are further treated at a temperature approaching the T_m for a short time (e.g., 1 min) and then rapidly quenched to room temperature for the subsequent TEM observation. If the spherulites consist of two crystal populations, the dominant and subsidiary components, as suggested by Bassett and Vaughan using two-stage replica method,[22] then the less perfect (or less stable) crystals should disappear (be melted) upon treating at temperatures higher enough. And, only the more perfect (or stable) ones are expected to remain upon the subsequent TEM observation. For this purpose, the initially cold-crystallized sample (having the same thermal history as in Figure 1) is further treated at 207 °C for 1 min and then rapidly quenched to room temperature for TEM observation. Most interestingly, it can be observed that many intact lamellae seen in the initial spherulites (see Figure 1) become segmented and disconnected although the spherulitic outline still remains (Figure 2), indicating that the thermal stability along single lamellae is not uniform. Despite the uniformity in lamellar appearance, within an individual lamella some parts are more stable or perfect than the others due to the difference in distribution of lamellar perfection. The melting event may be initiated from some weakened locations along the lamellae, such as structural defects, impurities, or elastically curved portions (with higher free energy resulting in melting point depression).[23] When further increasing the temperature of the partial melting experiment, for instance, to 215 °C for 1 min, it can be clearly observed that more lamellae with less thermal stability are melted, and only a few fractions are left (Figure 3A). Consequently, the remaining morphological details become much pronounced due to the removal of some less stable crystals. One main feature presented in Figure 3A is that the remaining lamellae become more isolated with increased distances, convincingly indicating the existence of subsidiary crystals (with lower thermodynamic stability) within the framework of the dominant populations.[22,24,25]

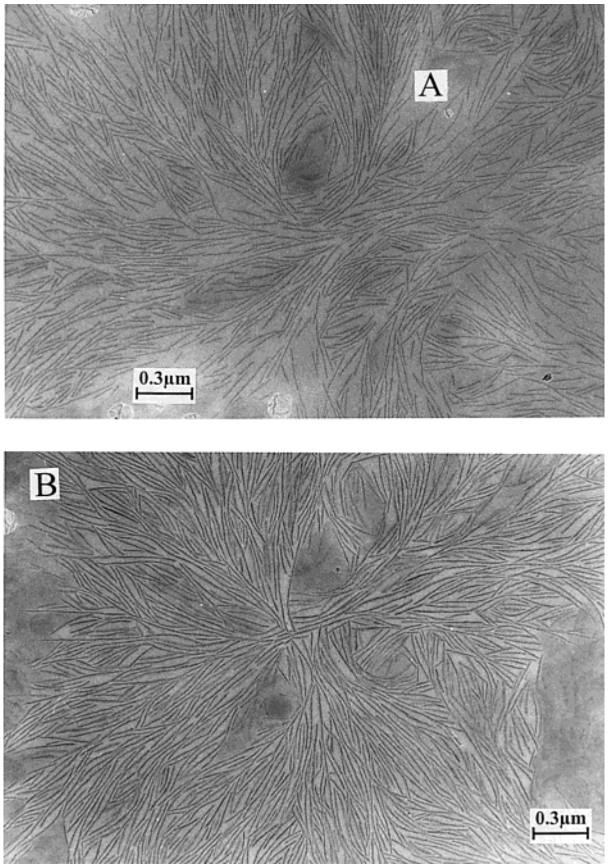

Figure 3. TEM BF electron micrographs of iPS samples having the same thermal history as in Figure 1, but subsequently treated at 215 °C for 1 min (A) and 30 min (B) before being quenched to room temperature.

Thus, from the TEM observations we have to conclude that, besides the presence of dominant and subsidiary crystals in spherulites, along *single* lamellae the thermal stability is even different. The less perfect (or defective) parts probably serve as nuclei of melting of the lamellae. Very interestingly, similar observation was also made recently in lamellar single crystals of syndiotactic polypropylene (s-PP) by Cheng and co-workers using TEM and hot-stage atomic force microscopy (AFM).[26] Accordingly, this is probably a common observation in semicrystalline vinyl polymers. The cause of such an observation is due to uneven distribution of tacticity along polymer chains which leads to one domain with relatively lower tacticity and other locations with higher tacticity. In the beginning of crystallization, the molecules with higher tacticity will crystallize first, and those molecules with lower tacticity will be first rejected and accumulated in the front of crystal growth. Later on, as soon as these enriched molecules are too many and cannot diffuse away quickly enough, they have to crystallize to form less perfect crystals. These defective or less perfect crystals accumulated in certain locations possess relatively high free energies (that destabilize the crystals) and provide nuclei for the

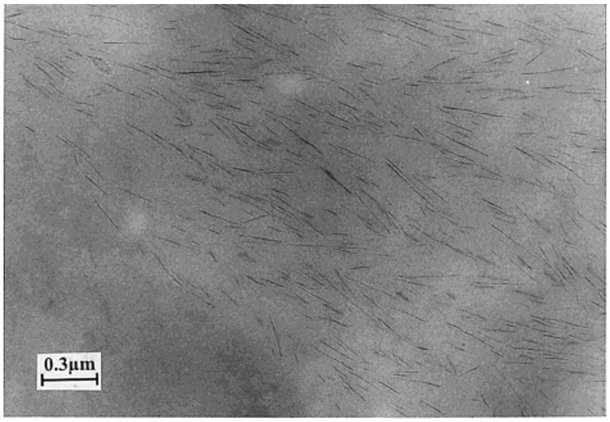

Figure 4. TEM BF electron micrograph of an iPS sample having the same thermal history as in Figure 1, which was further thermally treated at 220 °C for 1 min and then quenched to room temperature.

crystal melting event. Therefore, it is segregation during crystallization process that would be responsible for the local melting of lamellar domains with different thermodynamic stability.

To study the possibility of recrystallization after partial melting, the originally crystallized sample is kept at 215 °C for a long period of time, here, 30 min. As illustrated in Figure 3B, the "destroyed" disconnected lamellae (seen in Figure 3A) are "repaired" due to the reorganization (i.e., melting−recrystallization) process by laterally growing and, finally, become a nearly connected lamellar structure again. Such a repairing phenomenon of the molten domains (via a recrystallization process while annealing at higher temperature for an extended period of time) was also observed in s-PP by Cheng and co-workers.[26] Additionally, in contrast to Figure 3A, a lamellar thickening process can be obviously observed, indicating a competition between melting and recrystallization processes. The degree of lamellar fragmentation becomes much less evident due to the dominance of recrystallization process under the used treatment. When the partial melting experiment is carried out at an even higher temperature, for example, 220 °C for 1 min, the last trace of lamellar melting is imaged as presented in Figure 4. It shows that most of the lamellae are melted, and only a very small fraction of relatively straight lamellae remain.

In conclusion, we have demonstrated that TEM provides a direct visualization of how the melting and the structural rearrangement (via recrystallization) processes occur on the nanoscale in iPS spherulites. The presence of the dominant and subsidiary lamellae is directly confirmed by morphological observations. Most significantly, the thermodynamic stability within single lamellae is not uniform due to structural fluctuation as reflected by the fragmentation of lamellae upon thermally treating at different temperatures. The less perfect domains along an individual lamella serve as melting nuclei. The occurrence of repairing of molten domain via recrystallization is evidenced by the TEM observations. Therefore, a series of morphological observations provide a more complete description and better understanding on the internal organization of polymer crystals, reflected by the difference in thermal stability of the lamellae upon experiencing different thermal history. But care should be taken to generalize our observations from the iPS to other polymers. Because of different segmental mobility, chain conformational defects, and diffusive processes, different crystallization and melting events may occur in different polymers.

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References and Notes

(1) Bassett, D. C. *Principles of Polymer Morphology*; Cambridge University Press: Cambridge, 1981.
(2) Wunderlich, B. *Macromolecular Physics*; Academic Press: New York, 1973; Vol. 1.
(3) Keller, A.; Kolnaar, J. W. H. *Prog. Colloid Polym. Sci.* **1993**, *92*, 81−102.
(4) Hobbs, J. K.; Miles, M. J. *Macromolecules* **2001**, *34*, 353−355.
(5) Liu, T. X.; Lieberwirth, I.; Petermann, J. *Macromol. Chem. Phys.*, in press.
(6) Vaughan, A. S.; Bassett, D. C. In *Comprehensive Polymer Science*; Booth, C., Price, C., Eds.; Pergamon Press: New York, 1989; Vol. 2, Chapter 12, pp 415−457.
(7) Lavine, M. S. *Science* **2001**, *291*, 949.
(8) Li, L.; Chan, C. M.; Li, J. X.; Ng, K. M.; Yeung, K. L.; Weng, L. T. *Macromolecules* **1999**, *32*, 8240−8242.
(9) Li, L.; Chan, C. M.; Yeung, K. L.; Li, J. X.; Ng, K. M.; Lei, Y. *Macromolecules* **2001**, *34*, 316−325.
(10) Edwards, B. C.; Phillips, P. J. *Polymer* **1974**, *15*, 351−356.
(11) Sikes, H. D.; Schwartz, D. K. *Science* **1997**, *278*, 1604−1607.
(12) Magonov, S. N.; Elings, V.; Papkov, V. S. *Polymer* **1997**, *38*, 297−307.
(13) Pearce, R.; Vansco, J. *Polymer* **1998**, *39*, 1237−1242.
(14) Pearce, R.; Vansco, J. *Macromolecules* **1997**, *30*, 5843−5848.
(15) Schultz, J. M.; Miles, M. J. *J. Polym. Sci., Polym. Phys.* **1998**, *36*, 2311−2325.
(16) Hobbs, J. K.; McMaster, T. J.; Miles, M. J.; Barham, P. J. *Polymer* **1998**, *39*, 2437−2446.
(17) Godovsky, Y. K.; Magonov, S. N. *Langmuir* **2000**, *16*, 3549−3552.
(18) Godovsky, Y. K.; Papkov, V. S.; Magonov, S. N. *Macromolecules* **2001**, *34*, 976−990.
(19) Bu, H. S.; Cao, J.; Zhang, Z. S.; Zhang, Z.; Festag, R.; Joy, D. C.; Kwon, Y. K.; Wunderlich, B. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 105−112.
(20) Liu, T. X.; Petermann, J. *Polymer* **2001**, *42*, 6453−6461.
(21) Petermann, J.; Gleiter, H. *Philos. Mag.* **1975**, *31*, 929−934.
(22) Bassett, D. C.; Vaughan, A. S. *Polymer* **1985**, *26*, 717−725.
(23) Petermann, J.; Gohil, R. M. *J. Macromol. Sci., Phys.* **1979**, *B16*, 177−192.
(24) Keller, A.; Cheng, S. Z. D. *Polymer* **1998**, *39*, 4461−4487.
(25) Cheng, S. Z. D.; Keller, A. *Annu. Rev. Mater. Sci.* **1998**, *28*, 533−562.
(26) Zhou, W.; Cheng, S. Z. D.; Putthanarat, S.; Eby, R. K.; Reneker, D. H.; Lotz, B.; Magonov, S.; Hsieh, E. T.; Geerts, R. G.; Palackal, S. J.; Hawley, G. R.; Welch, M. B. *Macromolecules* **2000**, *33*, 6861−6868.

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