

Integrated microscopic analysis of lamellar structure in isotactic polypropylene spherulite at nanoscale

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Isotactic polypropylene (iPP) is a semicrystalline thermoplastic polymer of significant commercial importance due to its favorable combination of ultimate properties which can be achieved at relatively low cost. Conventional melt-crystallization at low supercooling results in formation of crosshatched monoclinic lamellae and a spherulitic superstructure, with the crystallinity, thickness of lamellae, and size of spherulites being tunable through the crystallization temperature or the annealing temperature [1-2]. To optimize the preparation conditions of iPP spherulites, as well as to tailor the properties for commercial use, comprehensive analytical techniques are of great importance. In this paper, we demonstrate complementary nanoscale characterization techniques, by conducting a coordinated study involving atomic force microscopy (AFM), nanoscale infrared (IR) spectroscopy, chemical mapping and high resolution scanning electron microscopy (SEM) to probe the localized morphology, crystalline/amorphous interface, lamella structure and functional group distribution at the spherulites.

The iPP spherulite studied here was prepared by non-isothermal crystallization of the melt by cooling to 135 °C at a rate of 10 °C/min and then cooling to 100 °C at 1 °C/min. The diameter of most spherulites was about 100-200 μm. Fig. 1a shows an AFM height image of an α-iPP spherulite center with a scan area of 20 μm x 20 μm. To investigate the orientation of lamellae in different radial directions, we can acquire the localized IR spectrum with nanoscale resolution by positioning the AFM probe in a specific region. Note that the probe tip radius is approximately 35 nm, which is far below the conventional optical diffraction limit. As shown in Fig. 1b, the CH₂ bending, CH₃ symmetric, CH bend/ CH₃ rock/C-C stretching at 1434 cm⁻¹, 1370 cm⁻¹, 1167 cm⁻¹ in the IR spectrum are fingerprints of iPP. In addition, two absorption peaks at 998 cm⁻¹ and 973 cm⁻¹ can be ascribed to crystallinity [3]. A high resolution AFM height image (3 μm x 3 μm) of the cross-hatched lamellar structure at the spherulite edge is shown in Fig. 2c. It can be seen that the radial lamellae are dominant and 2–3 μm in length and 30 nm in lattice distance. The radial lamellae branches occasionally form tangential lamellae, as indicated by the arrow in Fig. 2c. Fig. 1d-f shows the AFM height images of a PP spherulite edge with a scan area of 2 μm x 2 μm and corresponding chemical mapping image at the fixed wavenumbers of 1370 cm⁻¹ and 998 cm⁻¹ respectively, showing the map for the CH₃ symmetric bending, and crystallinity distribution.

Fig. 2a shows a low-mag SEM image of an iPP spherulite covering the region from the center to the edge. A fully developed spherulite can be clearly discerned. Fig. 2b shows the enlarged region of spherulite edge marked in Fig. 2a. The high-mag enlarged red (Fig. 2c) and blue (Fig. 2d) regions of the spherulite edge marked in Fig. 2b clearly shows the lamella texture. The crosslinked and parallel lattice distance is ~15 nm. It is apparent that the spherulite comprises radiating and space-filling branches of chain-folded lamellar crystallites. The lamellar texture of the 15 nm layers varied somewhat from one area to another. Upon close inspection, the fans were interspersed with areas of crosshatched lamellae and numerous short lamellar fragments, as shown in Fig. 2d. Our results also indicate that the lamellar textures observed by SEM are in agreement with image (Fig.1c) obtained by AFM. Future work will be focused on AFM

nanindentation to investigate the nanoscale mechanical properties as well as the localized morphology and property of oriented iPP crystalline structures.

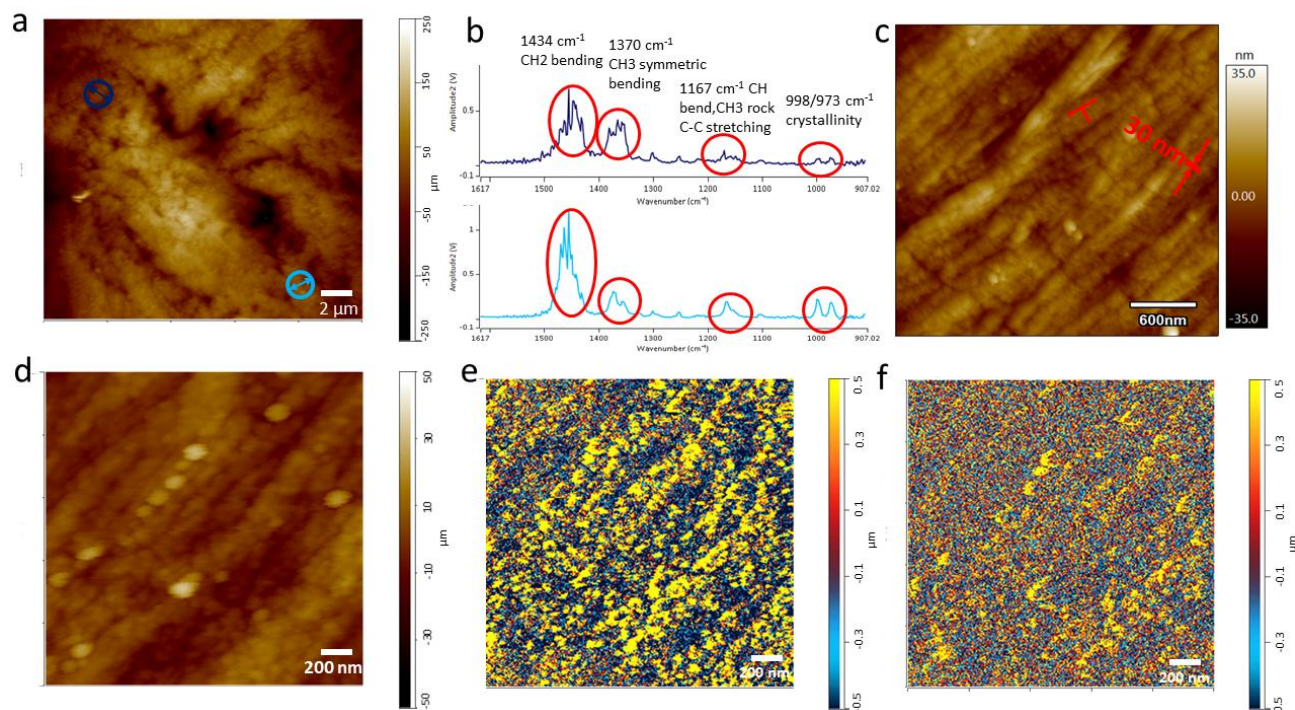


Figure 1. Fig. 1 (a) AFM topography image of polypropylene spherulite center with a scan area of 20 μm x 20 μm; (b) Localized nanoscale IR spectra at two single regions marked in Fig. 1a; (c) AFM topography image of polypropylene spherulite edge with a scan area of 3 μm x 3 μm; (d-f) AFM topography image of polypropylene spherulite edge with a scan area of 2 μm x 2 μm and corresponding chemical mapping image at the fixed wavenumbers of 1370 cm⁻¹ and 998 cm⁻¹ respectively, showing the map for the CH₃ symmetric bending, and crystallinity distribution.

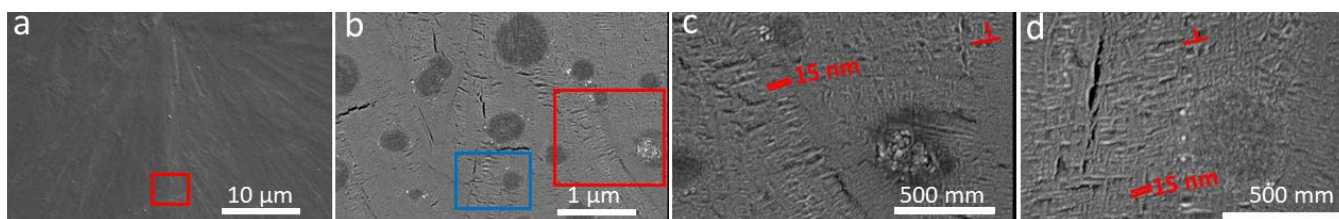


Figure 2. Fig. 2 SEM images of (a) polypropylene spherulite edge; (b) enlarged region of spherulite edge marked in Fig. 2a; (c) enlarged red region of spherulite edge marked in Fig. 2b; (d) enlarged blue region of spherulite edge marked in Fig. 2b.

References

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