



The structure of uniaxially stretched isotactic polypropylene sheets: Imaging with frequency-modulation atomic force microscopy



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ABSTRACT

Isotactic polypropylene sheets were uniaxially stretched and observed with a frequency-modulation atomic force microscope operated in phenyloctane liquid. Crystalline lamellae were seen in fibrils with their axis parallel to the stretched direction. Individual CH₃ side-chains of three-fold helices were identified in the lamellae. Fragmentation of the lamellae was induced by further stretching. The real-space features observed with the microscope were successfully compared with X-ray scattering results obtained in a synchrotron radiation facility.

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1. Introduction

Crystalline polymers can appear as hierarchical structures ranging from crystal lattices to spherulites. The hierarchical structures in a polymer object are affected in particular by tacticity, molecular weight distribution, and manufacturing processes. X-ray scattering provides a powerful tool to characterize these hierarchical structures [1,2]. Using a high-brilliance X-ray beam available at synchrotron radiation facilities, it is possible to trace scattering patterns on a sub-second-order time resolution, thus providing information on crystalline structure deformation dynamics during isothermal crystallization [3,4], stretching [5,6] and spinning processes [7,8]. On the other hand, X-ray scattering provide only generalized structural information that is averaged over the area irradiated with the X-ray beam, the diameter of which is on a micrometer-scale using the highly advanced microbeams available at synchrotron radiation facilities [9,10]. Polymer crystals are often heterogeneous, making it necessary to use real-space imaging to create a full picture of polymer objects. Atomic force microscopy (AFM), which provides topographic images on a nanometer-scale

resolution, is a promising development for this purpose. At present, only a few studies have used this technique to observe polymer chains and fold-chain lamellae [11–16]. By using these techniques complementarily, there is great potential to research polymer structures in detail.

Zuo et al. [17] revealed structural changes in isotactic polypropylene (iPP) sheets uniaxially stretched to different extents at different temperatures by combining small-angle X-ray scattering (SAXS), wide-angle X-ray scattering (WAXS), and AFM: spherulites transformed into fibrils along the stretched direction. Moreover, by analyzing in-situ X-ray scattering patterns, they found deformation of the crystal and amorphous phases during uniaxial tensile deformation at both low and high temperatures.

Recent developments in AFM technology have been focused on high-resolution imaging of soft materials. Mullin et al. [18,19] observed polyethylene single chains in air by tapping them with T-shape cantilevers and measuring their torsional oscillation. Fukuma et al. [20] developed low-noise sensing of cantilever deflection in frequency-modulation AFM (FM-AFM), and imaged mica in water at a true atomic resolution. Force sensing in the frequency-modulation scheme enables imaging scans with limited tip-surface force and hence less invasive scans over soft objects. A number of soft materials have been imaged with liquid-compatible FM-AFM to date, including crystalline *p*-nitroaniline [21], rubrene

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[22], lysozyme [23], dodecanol adsorbed on graphite [24], hydrophilic thiolate monolayers on gold [25,26], lipid bilayers [27], purple membranes [28], peptide nanotubes [29], antibodies [30], and DNA [31]. As synthetic polymers, commercial sheets of polyethylene [32] and polypropylene [33] have also been imaged in liquids. In these previous works, the molecular-resolution images were obtained without using a Fourier filter. Therefore, in this study, the aim was to observe how the single chains in uniaxially stretched iPP sheets are imaged by liquid-compatible FM-AFM and compare the observations with X-ray scattering results.

2. Experimental section

Isotactic polypropylene (iPP) sheets were prepared by pressing a commercial iPP product (Sigma–Aldrich; number average molecular weight: 67,000 weight average molecular weight: 2,50,000). Purchased pellets were melted at 473 K for 5 min and pressed 10 MPa using a hot press, then quenched at 293 K. The prepared sheets were mounted between two clamps of a tensile instrument and uniaxially deformed while measuring the load. The engineering stress σ is the load divided by the initial cross section, and the strain ε is defined $\varepsilon = 100(l - l_0)/l_0$ with l_0 and l as the initial and final lengths of the sample, respectively. The initial length l_0 was 12 mm in this study. Uniaxial stretching measurements were carried out at 393 K with a stretching rate of 10% per min. In-situ SAXS and WAXS measurements were performed at the BL03XU of SPring-8 [34]. The radiating X-ray was monochromatized to be of a 0.1-nm wavelength and was introduced to the stretching film. The azimuth of the incident beam was perpendicular to the stretched direction. Small-angle scattering patterns were detected with an X-ray image intensifier with a cooled CCD, whereas wide-angle scattering patterns were collected on an X-ray flat-panel imager. The acquisition time was 2 s per frame.

The topography of the iPP sheets stretched by 0%, 200%, or 1500% was first observed in air at room temperature using a commercial AFM (Bruker, Multimode) operated in tapping mode using non-coated silicon cantilevers (Bruker, NCHV). Amorphous layers left on the press sheet ($\varepsilon = 0\%$) were stripped off by chemical etching [35]. The etching solution was prepared by dissolving KMnO_4 (280 mg) in concentrated sulfuric acid (12 ml) and carefully adding phosphoric acid (18 ml). The iPP sheets were immersed in the solution for 2 h at room temperature, then transferred to a solution of dilute sulfuric acid (water 12 ml + concentrated sulfuric acid 18 ml) and hydrogen peroxide (30 w/v%) for 30 min each, washed with distilled water, and dried in air. The stretched iPP sheets ($\varepsilon = 200$ and 1500%) were imaged without chemical etching.

The iPP sheets stretched by 200% or 1500% were then further imaged in phenyloctane liquid using another AFM (Shimadzu, SPM9600) modified for highly sensitive frequency-modulation sensing of tip-surface force. Silicon cantilevers backside-coated with aluminum (Nanosensors, NCH-R) were used. Phenyloctane was chosen for the imaging liquid since it does not dissolve iPP and has low volatility.

3. Results and discussion

Fig. 1 shows the stress–strain curve of an iPP sheet observed under uniaxial tensile deformation at 393 K with selected 2D WAXS and SAXS patterns. The stress was proportional to applied strains of up to 15% showing an elastic response of the stretched sheet. Beyond the yield point of 15%, plastic deformation occurred with a gradual increase of stress until the sheet fractured at 1600%. In the absence of strain, five Debye–Scherrer rings appeared in the WAXS pattern. An iPP polymer chain appears as a three-fold helix (3_1 helix) with a repetition length of 0.65 nm along the helix axis [36].

Four polymorphs of crystalline iPP are known: the monoclinic α -form (i.e., the dominant population), hexagonal β -form, orthorhombic γ -form, and smectic forms [37]. According to the scattering vector lengths q , the five rings observed in the WAXS pattern were assigned to diffractions of randomly oriented (110) at $q = 10.1 \text{ nm}^{-1}$, (040) at $q = 12.0 \text{ nm}^{-1}$, (130) at $q = 13.3 \text{ nm}^{-1}$, (111) at $q = 15.2 \text{ nm}^{-1}$ and $(\bar{1}31)/(041)$ at $q = 15.6 \text{ nm}^{-1}$ in the α -form. (The lattice spacing of $(\bar{1}31)$ and (041) of iPP α -form are much the same.)

By applying strains beyond the yield point, a limited portion of each diffraction ring strengthened, resulting in an arc presentation. All (hk0) arcs, including (110), (040), and (130), transformed into diffraction peaks with further strain increases. The azimuth of the peaks was perpendicular to the stretched direction. In addition, the off-axis arc overlapped with (111) and $(\bar{1}31)/(041)$. These results are consistent to earlier studies [6,17,38] and suggest that plastic deformation induced crystallization in the α -form with the c -axis parallel to the stretched direction.

In crystalline polymers, crystalline lamellae should coexist with amorphous domains. Crystalline areas are generally more densely packed than amorphous areas, and the electron density of the crystalline lamellae is slightly larger than that of the amorphous domains. X-ray scattering in the domains of different electron densities contributes to an SAXS pattern. Accordingly, the average size of the domains can be estimated by analyzing the SAXS patterns. The observed SAXS patterns started with a broad isotropic ring, suggesting randomly oriented stacking of lamellae. A bright area appeared at the center with a strain of 30% and transformed into an equatorial streak with increasing strain until the sheet fracture. Two additional diffractions were generated at the top and bottom of the original ring. Both the WAXS and SAXS patterns suggested the presence of lamellar stack along the drawing direction. Fig. 2 shows the 1D SAXS profiles of the iPP sheets stretched by 200% and 1500%. The curves are integrated from the meridian region. A broad peak centered at $q = 0.29 \text{ nm}^{-1}$ was observed at 200%, which indicates a periodic structure with a center value of 21.7 nm along the direction of stretching. On the other hand, when stretched by 1500%, there was no distinct peak. Further stretching resulted in crystallization from interlamellar coiled segments or fragmentation of crystalline lamella, and the periodic structure observed at 200% disappeared.

Fig. 3 shows the ex-situ AFM topography of another iPP sheet stretched at different strains. The topography of the sheets was observed in air at room temperature using a commercial AFM operated in tapping mode. In the topography of the unstretched sheet, which is shown in panel (a), radial structure and spherulites were recognized. The spherulites then transformed into fibrils when stretched, as shown in panels (b) and (c). The axis of the fibrils was parallel to the stretched direction. The SAXS patterns shown in Fig. 1 presented qualitatively different features at strains of 200 and 1500%. The diffractions at the top and bottom of the ring were present at 200% and absent at 1500%. However, the topography of the sheets stretched to these extents (shown in Fig. 3(b) and (c)) displayed similar features even when zoomed into small areas of the scan. This finding suggests that the spatial resolution of the microscope was not sufficient to recognize the topographic response related to the SAXS results. Hereafter, we employed FM-AFM to identify polymer-chain-scale features exposed on the iPP surfaces.

Fig. 4 presents FM-AFM images of the stretched iPP sheet. When a solid object approaches a cantilever oscillating in mechanical resonance, the resonance frequency shifts due to the conservative force pushing or pulling the tip at the free end of the cantilever. The tip-surface distance is feedback-regulated to keep the shift of resonance frequency (Δf) constant. In ordinary operations of FM-

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