Surface Morphology and Frictional Property of Polyethylene Single Crystals Studied by Scanning Force Microscopy

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Since the polyethylene (PE) single crystal from a dilute xylene solution was discovered by Keller,[1] several folding models of a molecular chain in a PE single crystal have been proposed.[1,2] As the chain length of PE is much longer than the thickness of the lamellar crystals, a PE molecule should fold at the lamellar surface with an appropriate conformational change. However, since direct evidence supporting one chain folding structure over another has not been found, various possibilities for the chain folding structure have been discussed for the past three decades.[3–6] Also, the folding structure of a PE molecular chain strongly depends on the crystallization temperature, the cooling rate, the molecular weight, and its distribution.[6]

Scanning force microscopy (SFM) is one of the new scanning probe microscopic (SPM) techniques for investigating a material's surface with high spatial resolution.[7] SFM can image the surface morphology on the basis of the various types of forces acting between a sharp microcantilever tip and the sample surface, such as van der Waals, electrostatic, frictional, and magnetic forces.[8–10] Surface morphological observations of PE single crystals have been made by SPM.[11–13] However, no direct evidence has been obtained on the chain folding on the single-crystal surface. As the chain folding portion is in the amorphous state, the molecular imaging of chain folding might be very difficult. The friction force microscopic (FFM) technique might reflect the tribological properties and structure symmetry at the surface.[9] In this study, atomic force microscopic (AFM) observation was carried out to investigate the surface morphology of the polyethylene single crystal. Also, friction force microscopic (FFM) observation was carried out to evaluate the friction force parallel and perpendicular to the {110} growth face of the PE single crystal.

Experimental Section. The polyethylene used was high-density polyethylene (HDPE, Marlex 9, weight-average molecular weight $M_w = 520K$) with a broad molecular weight distribution and fractionated HDPE ($M_w = 10K$) with a narrow molecular weight distribution ($M_w/M_n = 1.02$). PE single crystals were prepared by isothermal crystallization. HDPE(M_w=10K) was dissolved in tetrachloroethylene at 393 K to obtain a 0.01 wt % solution. The solution was then kept at 343 K for several hours. Then the solution was cooled to room temperature. Also, HDPE(M_w=520K) was dissolved in xylene at 393 K and isothermally crystallized at 353 K for several hours. Then the solution was cooled to room temperature. A small amount of this solution liquid with suspended single crystals was dropped onto a cleaned silicon wafer surface and allowed to air-dry at room temperature.

AFM and FFM images of HDPE single crystals were obtained with an SPA300 instrument (Seiko Instrument Industry Co., Ltd., Japan). The cantilever used in this study is V-shaped with a silicon nitride (Si_3N_4) quadrangular pyramid microtip (Olympus Co., Ltd., Japan). The bending spring constant of the cantilever is 0.022 N m^{-1}. In the AFM and FFM observations, a feedback loop keeps the vertical position of the tip constant by moving the sample surface (the sample position) up and down with the piezoelectric scanner (topography mode). The images were taken with a 1 μm × 1 μm or 20 μm × 20 μm scanner. The AFM observation was carried out in air, and the applied force between the microtip and the specimen surface (force reference) was set between −0.021 (repulsive force) and 0.42 nN (attractive force). The FFM measurement was carried out under a force of −0.021 nN (repulsive force). In the FFM measurement, the magnitude of the anisotropic frictional force was measured by varying the scanning angle with reference to the {110} growth face of the PE single crystal. Figure 1 shows the definition of the scanning angle, θ, in the FFM measurement. In the measurement of the frictional force, the long axis of the cantilever is perpendicular to the scanning direction, and then the degree of the cantilever torsion reflects precisely the magnitude of the frictional force between the microtip and the sample surface. The scanning angle, θ, was varied from 0° (parallel to the {110} growth face) to 90° (perpendicular to the {110} growth face) by rotating the PE single crystal against the cantilever.

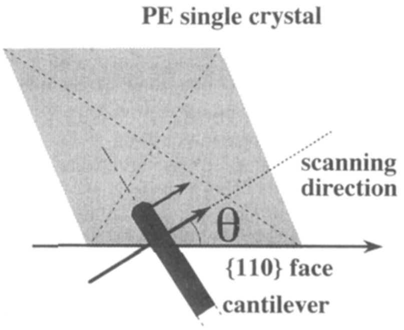

Figure 1. Schematic representation of the definition of the scanning angle, θ, in the friction force measurement.

Results and Discussion. Figure 2a shows the topographical image of the HDPE(M_w=10K) single crystal. Images were captured while scanning without filters. A characteristic lozenge-shaped lamellar crystal, ca. 5 μm long and ca. 10 nm thick, was observed. The thickness and dimension of single crystal agreed with those observed on the basis of small-angle X-ray scattering measurement and transmission electron microscopic observation,[6] respectively. Figure 2b shows the enlarged image of the {110} growth face, corresponding to the marked zone shown in Figure 2a. The pleats parallel to the {110} growth face (the direction of arrow A in Figure 2b) may suggest the orientation of the chain folding on the single-crystal surface. The *b*-axis ridge (the direction of arrow B in Figure 2b) which appeared along the sector interface might be formed due to the collapse of the hollow pyramid structure.

The frictional curve was measured to reveal the regularity of chain folding on the PE single-crystal surface. We assumed that, depending on the scan direction of the cantilever tip, it might experience lower friction when the tip is slid along fold loops parallel to the {110} growth face or higher fraction when the tip is bumped into the fold loops. The magnitude of the frictional force was measured at various scanning angles with respect to the {110} growth face. Unfortunately,

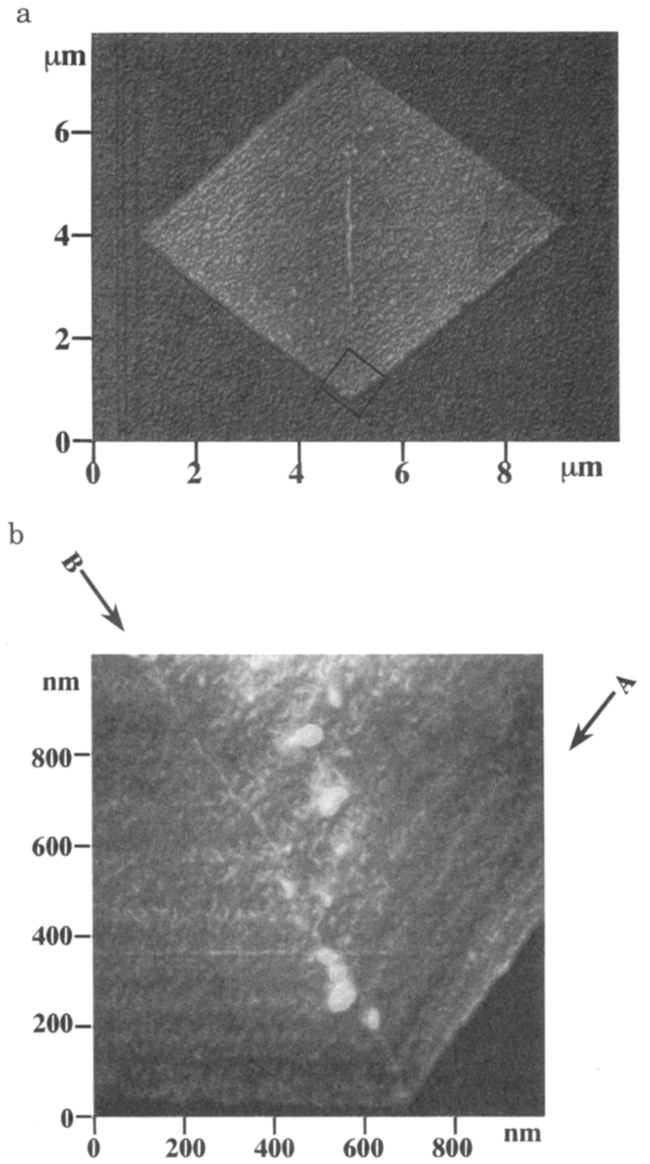

Figure 2. (a) AFM image of fractionated HDPE(M_w=10K) single crystal and (b) enlarged image of the edge part of (a).

the absolute frictional force could not be evaluated since the contact area of the cantilever tip against the sample surface was not evaluated precisely. The magnitudes of the frictional force were estimated by the output voltage from a four-quadrant photodiode detection system. Since the frictional force was evaluated on the basis of the frictional curve under bidirectional scanning, the contribution from the topography to the frictional force can be determined.

Figure 3 shows the scanning angle dependence of the frictional force for PE single crystals with M_w = 10K and 520K. In the case of the single crystal of unfractionated HDPE(M_w=520K), the magnitude of the frictional force was independent of the scanning angle, θ. This result indicates that a regular direction of the chain folding is not present on the single-crystal surface of unfractionated HDPE with M_w = 520K. On the other hand, in the case of a single crystal of fractionated HDPE(M_w=10K), the magnitude of the frictional force increased gradually with the scanning angle, θ, from 0 to 90°. This means that a regular chain folding direction exists on the PE single-crystal surface. The magnitude of the frictional force was larger for the HDPE single-crystal surface with M_w = 520K than that with M_w = 10K. These facts strongly suggest that switchboard-like random loose loops are formed on the HDPE single-crystal surface with M_w = 520K, whereas sharp and regular folds are present on the HDPE single-crystal surface with M_w = 10K and a narrow molecular weight distribution.

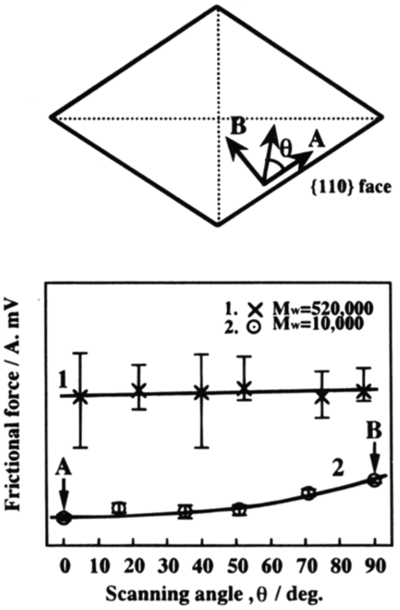

Figure 3. Scanning angle dependence of the frictional force for HDPE single crystals with M_w = 10K and 520K.

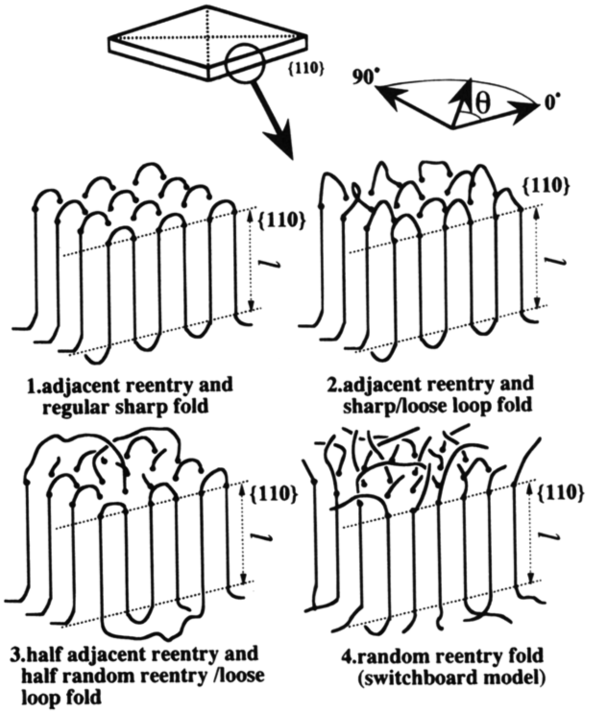

Figure 4. Schematics of conceptual chain folding structures of PE single crystals.

The nature of the PE single-crystal surface at which the polymer chains emerge, fold, or reenter has been the subject of considerable controversy.[2-5] Figure 4 shows schematics of four conceivable chain folding structures on the PE single-crystal surface. Structure 1 shows that chain folds back with minimal loops and also with high probability of adjacent reentry. On the other hand, structure 4 shows that the reentry occurs more or less at random with loops with much longer than the minimal size. Structure 2 shows that the chain folding has adjacent reentry but some loops are much longer than the minimal size. Structure 3 is an intermediate one between structures 1 and 4. The anisotropy of the frictional force against the scanning angle, θ, may reflect the regularity of the chain folding direction. Therefore, it seems reasonable to conclude that PE single crystals from unfractionated HDPE with M_w = 520K have a switchboard-like random loose loop (structure 4 in Figure 4) because of an almost isotropic frictional force on the scanning direction. On the other hand, the single crystal prepared from fractionated HDPE with M_w = 10K has a sharp regular fold surface (structure 1 or 2 in Figure 4) with an anisotropic frictional force.

In conclusion, the AFM observation directly revealed the pleats and ridge on the single-crystal surface of PE. The FFM experiment revealed that the magnitude of the frictional force in a sector of a PE single crystal was dependent on the scanning direction with respect to the {110} growth face in the case of PE single crystals prepared from fractionated HDPE with molecular weight of 10K and a narrow molecular weight distribution. On the other hand, the magnitude of the frictional force did not depend on the scanning direction in the case of PE single crystals prepared from unfractionated PE with M_w = 520K. These results are consistent with the assumption of a regular sharp fold for PE single crystals with M_w = 10K and the switchboard-like random loose loop for PE single crystals with M_w = 520K.

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