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Scanning Probe Microscopy of Poly(p-phenylene benzobisthiazole)Lamellar Crystal

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Rigid polymer, poly(p-phenylene benzobisthiazole), formed lamellar crystals where the molecular chains were oriented perpendicular to the lamellae. It was supposed that, because of wide distribution in the chain length, the lamellar surface bristled with the chain cilia among which many voids were included. Crystallographically, this region afforded us a transitional structure from full to deficient packings of chains. The structure was analyzed using the scanning probe microscope. In the course the method for imaging one molecular chain end was developed. From the images it was concluded that an isolated long cilius did not move so violently at room temperature.

1. INTRODUCTION

Flexible crystalline polymers form lamellar crystals when crystallized from dilute solution. Experimental studies have shown that in the crystals each molecular chain folds back and forth several times with constant fold length which does not depend on molecular chain length [1,2]. Arrangement of the fold on the lamellar surface was examined by the scanning probe microscopy (SPM) [3,4,5].

Poly (p-phenylene benzobisthiazole) (PBZT) is a rigid crystalline polymer and the molecular chains can not fold. The so-called PBZT single crystals have been prepared from dilute solution [6,7]. Their morphologies are strongly dependent on the molecular length and its distribution. Shorter PBZT chains crystallize into a lozenge lamellar crystal where the rigid chains of different length are accommodated perpendicular to the lamella. A question of what happens to the chain end portions in this case remains as an essentially unsolved problem. In the work reported here a modified SPM method will be presented which enables the chain-end positions to be identified, suggesting a possibility of characterization of chain end motions.

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2. EXPERIMENTAL

2.1 Materials

PBZT polymer was synthesized according to the method of Wolfe et al. [8]. Intrinsic viscosity of the product was 3.4 dl/g from which average molecular length was estimated to be 54 nm from Berry's equation [9]. The solvent used for crystallization was 92% sulfuric acid. PBZT was put into the solvent (at concentration of 0.1 %), heated slowly to 105℃, then crystallized by slow cooling (cooling rate:0.1℃/min). This procedure was carried out under dry nitrogen to ensure an inert atmosphere.

2.2 Transmission electron microscopy (TEM)

The precipitates were roughly separated from H_2SO_4 by decantation and rinsed with distilled water several times. PBZT crystal suspension in water dropped onto carbon grids for TEM observation allowing water to evaporate. TEM image and selected area electron diffraction (SAED) were taken on JEM 200EX (JEOL, Tokyo, Japan) operated at 200kV and recorded on FUJI FG film. SAED pattern was taken at a camera length of 30 cm from area of 1-2 μm in diameter. The camera constant was calibrated by measuring d-spacing of gold evaporated onto selected specimens.

2.3 Scanning probe microscopy (SPM)

SPM image was taken in air on NanoscopeⅢa (Digital Instruments, Inc.). The probe and cantilever used were microfabricated silicon single crystals (Nano Probes, Digital Instruments, Inc., cantilever length: 450 μm, spring constant: 0.02-0.1 N/m, resonance frequency: 6-20 kHz, nominal tip radius of curvature: 5-20 nm). In this instrument, deflection of the probe was measured by change in direction of a laser beam reflected from the cantilever. Two different ways were adopted for imaging. One was the ordinary tapping mode where the piezo (the sample holder) responds to root-mean square (RMS) of the cantilever deflection signals by moving the sample up and down to keep the cantilever vibration amplitude constant (servomechanism). Another way was that the scanning was carried out without operating the servomechanism, i.e., with keeping the sample holder at constant height and constant input energy for cantilever vibration, while the deflection signals (RMS of cantilever deflection) were directly sent to the display for imaging. Here significance of this image exists only at area recorded by less energy transfer between the cantilever tip and the specimen. Several tens scannings with consecutive input energy were necessary for detecting many chain ends at different height for constructing a 3-dimensional image of the chain end distribution.

Imaging was reliable only when the scanning was slow enough for the tip to catch up with protrusions and dents. Actually by observation with the speed faster than 30Hz, resultant image smeared along the scanning direction. So we adopted 20Hz as the scanning speed.

3. RESULTS and DISCUSSION

3-1 Crystalline core in PBZT lamella observed by TEM

Transmission electron micrograph of a lozenge PBZT lamellar crystal is shown in Fig.1. At the center of the lamellar crystal there is a protruded region less than 15 nm in diameter. In addition, a protruded line ca.8nm wide extended along the diagonal. It is plausible that the protrusions acted as nuclei during the crystallization. Thickness of the lamellar edge, as determined from the width of platinum-palladium shadowing, was 54 nm, which was slightly less than the average chain length estimated from intrinsic viscosity.

Analysis of SAED pattern revealed that the lamella was composed of twin crystallites and that molecular chains oriented perpendicular to the lamella. This, coupled with the knowledge that the molecular chains were completely rigid and the chain length was polydisperse, suggested that the lamellar surface bristled with rigid chain cilia of different length.

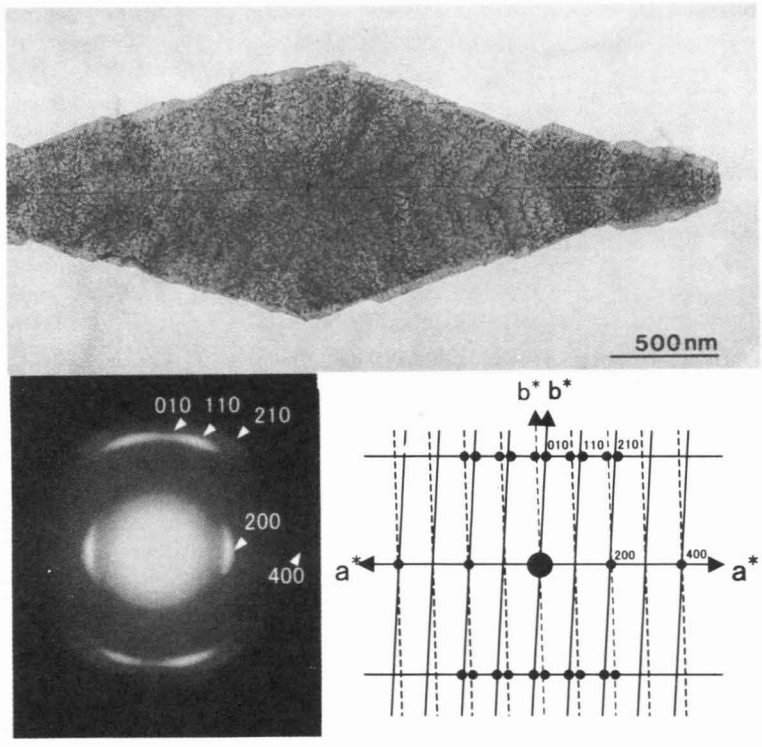

Fig.1 TEM of lozenge PBZT lamellar crystal and its SAED with reciprocal lattice.

3-2 Structure of transitional region from the crystalline core to the lamellar surface

The lamellar surface was observed with SPM in the ordinary tapping mode. Average height variation was measured along a line (A-B) drawn on Fig.2. Bumps and dents on

the lamella on a scale of from several to a few tens nanometers across and from less than one to a few tens nanometers high were evident. It should be noted that rows of bumps developed from the diagonal line at an angle of 60 degree, appearing like a fish bone. It seems that the rows grew dendrically along 310 direction then the crevices were filled up later.

Here we have to examine the meaning involved in this image. By the tapping mode, the cantilever deflection signals expressed as RMS was fed back to the piezo controller in order to compensate the difference from the prescribed value. Voltage applied to the piezo controller for the compensation was monitored as height information and sent to the display. The drawback of this process was that the piezo controller responded slower with smaller the prescribed value (concomitantly RMS). Consequently we usually set a large value as the prescribed value in order to take a clear image. Thus RMS for a clear image was obtained only when more than tens cilia interacted simultaneously with the tip because the tip of the cantilever was much thicker and much heavier than a cilius. So the image represented a layer of fairly populated cilia. Here most chains were inevitably deformed by the tip during detection (Fig.3). If we control the tapping force, the layers with various chain density will be imaged. Small stimulus to the cantilever tip such as that from one chain cilius was too small for the piezo to respond promptly for imaging in this ordinary tapping mode.

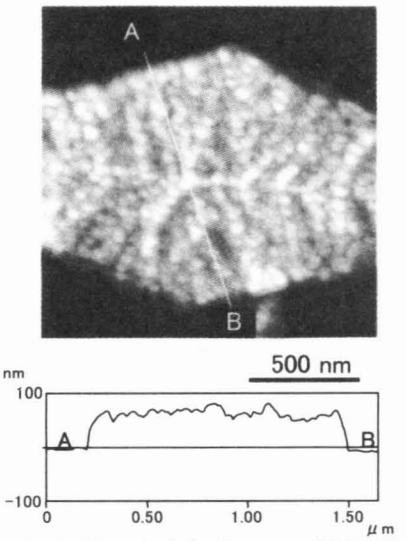

Fig.2 SPM height image of PBZT lamellar crystal surface taken in the ordinary tapping mode. The cross-sectional height profile along the line A-B is shown below the image.

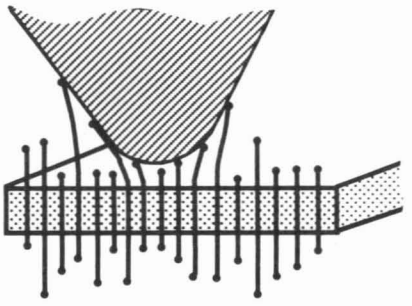

Fig.3 Schematic illustration of rigid chains deformed by the tip of the cantilever during observation by the ordinary tapping mode

3-3. Observation of sparse cilia on PBZT lamella

In order to image one cilius with weaker deflection signals, we had better send the original RMS directly on the display as a function of X and Y. Then the delay in response through the servomechanism can be eliminated. Fig.4 illustrates how the cilia can be detected as a function of the cantilever vibration amplitude. With a small vibration amplitude (Fig.4a), the vibration is deflected only by a longer cilius B, but not by another cilius A, thus only B can be recorded on the map. With increase in the amplitude (Fig.4b), the cilius A also begins to interfare the vibration, i.e., both are recorded on the map. Fig.5a shows one of the maps. For comparison, the image of the same area taken in the ordinary tapping mode is also shown in Fig.5b. It is clear

that islands such as A, B etc. in Fig.5a are observed to locate at positions of the corresponding bumps. Broad area B came from a longer cilius (or it might come from several cilia). On the other hand, Point A is a position where the tip slightly touched a cilius. By changing input energy for the cantilever vibration, several tens consecutive images were obtained. Reproducibility was ascertained by the fact that the features appeared at the same positions with the same sizes by decreasing and again by increasing amplitude of the cantilever vibration.

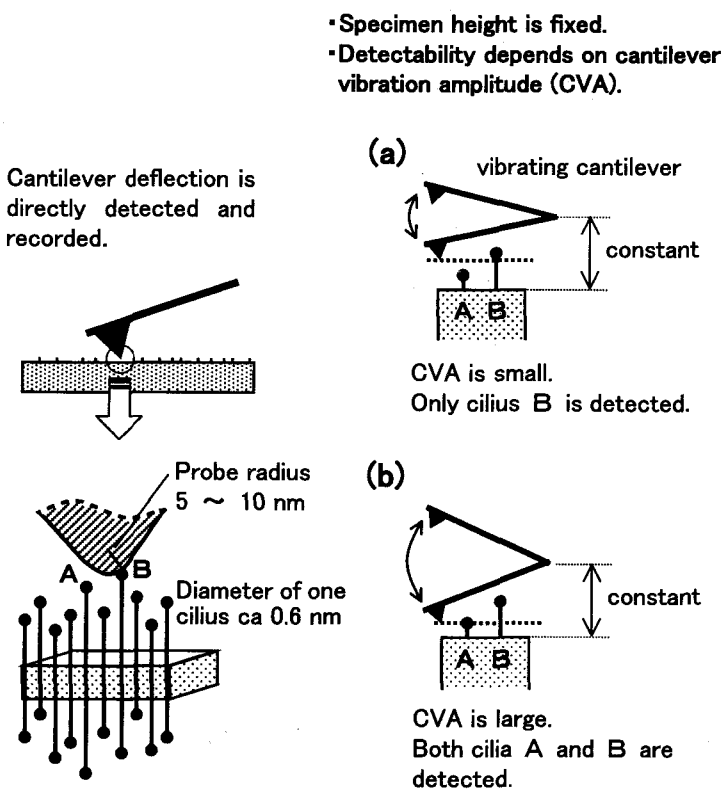

Fig.4 Schematic illustration of geometry between the amplitude of cantilever vibration and cilia on PBZT lamella

Fig.5c is a bird's-eye view of Fig.5a where A looks like a bamboo shot. The form resulted from convolution of shapes of the chain end and the probe tip, so significant information is only limited to the top area of the bamboo shot.* Thus height difference among the molecular chains were determined resulting in the 3-dimensional chain end distribution. Another important information is capability of detection of chain end motion as an image. For example, the cilius A, which was at least 15 nm long and standing solitarily, might rotate or vibrate thermodynamically at room temperature. But as the point A was observed to be less than 3 nm in diameter, it was concluded that this cilius was not moving so violently at 20 ℃. In addition, there is the possibility of detecting what chemical groups exist at the chain ends, by chemical modification of the tip surface for increasing or decreasing in affinity between the tip and the chain ends.

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* Here it should be examined whether the bamboo shot really constructed of only one cilius or a few cilia. As PBZT was prepared by polycondensation, it has broad distribution in molecular length. So two or more cilia seldom meet side by side at the same height.]

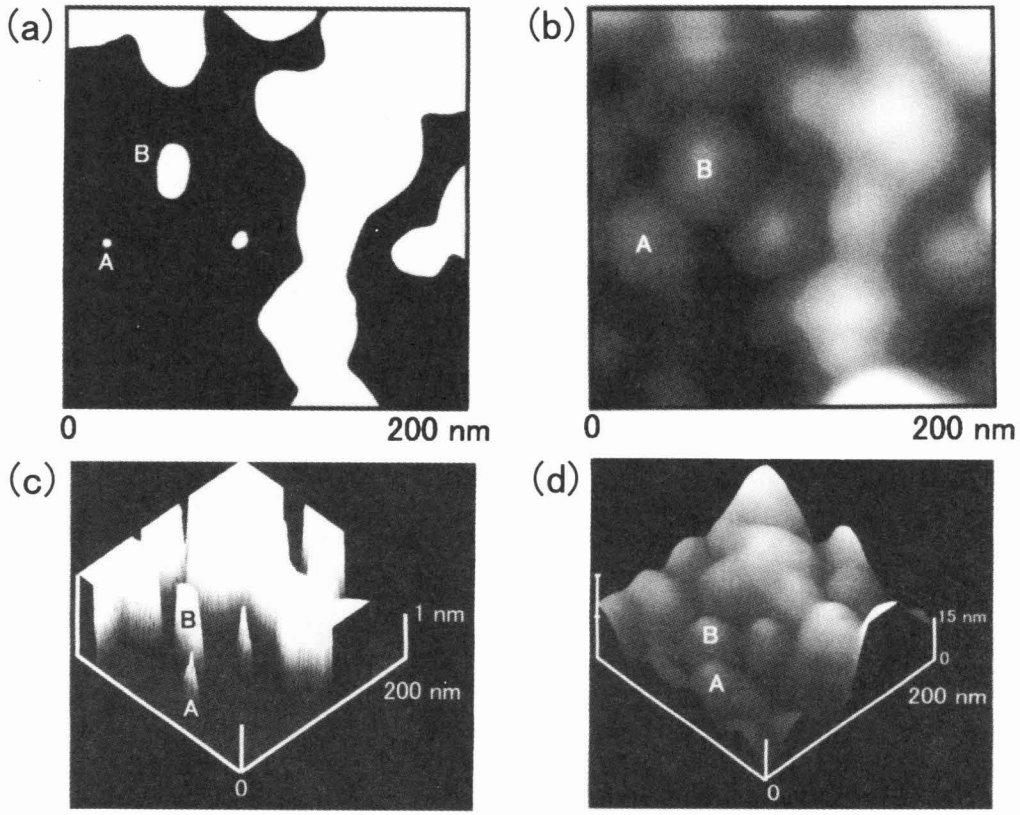

Fig.5 SPM height image of rigid cilia of different length on a PBZT lamellar crystal observed (a) by direct RMS mode, (b) by the ordinary tapping mode. The contrast covers height variations in the 0 – 2 nm in (a) and in the 0 – 30 nm range in (b).
(c) and (d) are bird's-eye views of (a) and (b) respectively.

4. CONCLUSIONS

A rigid polymer crystal, which has no chain folding but rigid cilia on the surface, was studied by TEM and SPM. In the analysis a new SPM mode was developed for imaging an isolated chain cilius. By combining the ordinary tapping mode with this mode, less perfect structural region with deficiency of molecular chains near the crystal surface was characterized.

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