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High-Resolution Observation of Crystal Transformation in Isotactic Polybutene-1 Single Crystals

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The crystal transformation in lamellar crystals of polybutene-1 grown from an amyl acetate solution was studied by cryogenic high-resolution transmission electron microscopy. The shape of the transformed trigonal (form-1) crystal domains in the surrounding tetragonal (form-2) crystal was successfully revealed. Along with the nucleation of "untwinned" form-1, the existence of another nucleation mechanism which creates "twinned" form-1 was suspected. The growth of form-1 crystal was thought to progress not stem by stem but by pulling in the molecular chains from the surrounding form-2, creating new stems of form-1. The shape of the form-1 domain was irregular, and no specific crystallographic direction along which the form-1 domain tends to grow was found.

Keywords : Transmission electron microscopy/ Lattice fringes/ Image processing/ Nucleation/ Molecular mechanism

Three major crystalline forms have been reported for isotactic polybutene-1 (PB1) so far. Form-1 is characterized by the trigonal unit cell (space group $R3c$ or $R\bar{3}c$; a = 1.77 nm, c (chain axis) = 0.65 nm) and 3/1 helical conformation of backbone chains. Form-2 has the tetragonal unit cell ($P\bar{4}$; a = 1.542 nm, c (chain axis) = 2.105 nm) in which four molecular chain stems with 11/3 helical conformation are packed. In form-3, molecular chains with 4/1 helical conformation are packed in the orthorhombic unit cell ($P2_12_12_1$; a = 1.238 nm, b = 0.888 nm and c (chain axis) = 0.756 nm). Form-2 gradually transforms into form-1 on aging at room temperature [1]. It is still unclear, in terms of the molecular movements, how form-2 transforms into form-1 without changing the original shape. In this paper, solution-grown lamellar crystals of PB1 are studied by high-resolution transmission electron microscopy (HREM). The shape of each crystal domain is discussed on the basis of the distribution of corresponding lattice fringes in the HREM image.

The as-received PB1 was dissolved in amyl acetate to be an 0.01 or 0.02 wt% solution. Isothermal crystallization was performed by putting a test tube containing the solution into an oil bath thermostated at the prefixed crystallization temperature. For HREM, a cryogenic transmission electron microscope (JEOL JEM-4000SFX; 400kV) was used. In this case, the built-in MDS was utilized and the specimen was cooled down to the liquid helium temperature (4.2K) to suppress electron irradiation damage [2,3]. The HREM images were processed with a computer for detection of the domains in which certain lattice fringes appear [4]. First, by applying a Fourier-filtering technique, an intermediate image was created from the original image using a pair of intensity maxima in the reciprocal space (viz., $hk0$ and $\overline{hk}0$; the origin, 000, was not included in processing). This intermediate image showed the corresponding lattice fringes on the whole area; the strength (contrast) of the lattice fringes was different from place to place. The intermediate image was

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Scope of research

Attempts have been made to elucidate the molecular arrangement and the mechanism of structural formation/change in crystalline polymer solids, polymer gels and elastomers, polymer liquid crystals, and polymer composites, mainly by electron microscopy and/or X-ray diffraction/scattering. The major subjects are: synthesis and structural analysis of polymer composite materials, preparation and characterization of polymer gels and elastomeric materials, structural analysis of crystalline polymer solids by direct observation at molecular level resolution, and *in situ* studies on structural formation/change in crystalline polymer solids.

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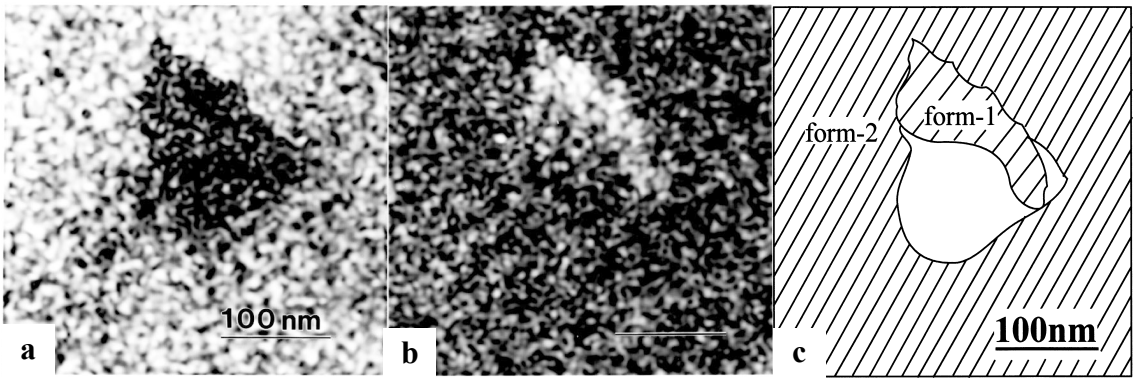

Figure 1. Partly transformed PB1 lamellar crystal. The specimen was kept at room temperature for 4 days before taking the HREM image. The bright regions are (a) form-2 and (b) form-1. The corresponding area and the orientation are summarized in (c), in which the stripes are drawn parallel to the (110) plane.

further processed by calculating the "local standard deviation" (LSD) of several (typically 5×5) pixels surrounding and including every given pixel. The LSD filter is a kind of smooth-edge detector and returns a larger value leading to an increase in brightness over a certain domain with inherent lattice fringes, namely lattice fringes that existed in the original image. By the image processing applied here, only the regions with inherent lattice fringes having a high contrast ought to be highlighted.

Figure 1 shows a set of images processed from one of the HREM images. The bright regions in parts a and b of Figure 1 show the form-2 and form-1 domains, respectively. Since the small spots in the processed images should have come from the noise in the original micrograph, they were neglected. Figure 1c summarizes the arrangement of these form-2 and form-1 domains. The stripes in each domain are drawn as to be parallel to the (110) plane. Because there is only one form-1 domain of single orientation, form-1 seems to have nucleated in a manner which does not include twinning.

Figure 2 summarizes the results from another set of processed images. It should be noted that four form-1 domains meet at one "point" indicated by the arrow in Figure 2. The convergence of separately-nucleated four domains at one "point" should be statistically rare. Furthermore, each pair of the two domains opposed at the "point" has the same crystallographic orientation. Therefore, it is strongly believed that the four form-1 domains nucleated at the point indicated by the arrow as a twin crystal. Figure 2 suggests that there is another nucleating mechanism which starts from a certain peculiar "point", creating the "twinned" form-1 crystallites.

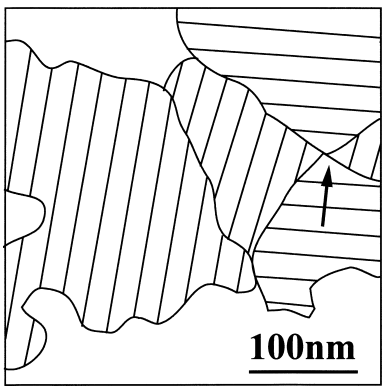

Figure 2. Arrangement of transformed form-1 crystallites in a lamella. The specimen was kept at room temperature for 4 days before taking the original HREM image. The stripes are drawn parallel to the (110) plane.

Because of the conformational change, the transformation from form-2 to form-1 accompanies the increase in length (by ca. 13%) of a molecular stem which is composed of a given number of monomer units. At the same time, the density of the crystallites increases and the area for a given number of stems decreases (by ca. 24% on the *ab*-plane). However, we observed neither the variation of lamellar thickness nor the generation of vacancies in the lamellae. Therefore, a considerable part of the increment of the stem length on the transformation should be consumed to fill the vacancy which results from the density change. The form-1 domain may grow by reeling in the molecular chains from the surrounding form-2 domain, uncoiling the form-2 crystallites and creating new stems of form-1. This hypothesis is supported by the fact that we found a region of several hundreds of nanometers of square, where three crystallites of the form-1 are closely packed without discernible vacancy. If the transformation were to progress stem by stem without changing the number of stems, then some of the stems would have to travel several tens of nanometers of distance (much more larger than the stem length) to form such a large crystallite.

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