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Structure image of single crystal of polyethylene

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Abstract

High-resolution electron macroscopic images of lamellar single crystal of polyethylene (PE) have been successfully obtained using high-resolution electron microscopy (HREM), although so far the feasibility of obtaining HREM images from such a radiation sensitive polymer is still drastically questioned. The HREM images with a clear two-dimensional periodic structure reported here were recorded in a transmission electron microscope operated at 200 kV. The images consisted of lattice fringes derived from the ⟨001⟩ zone, and the structure images of different lattice fringes were resolved. To our knowledge, this is the first time that such clear structure images of PE have been reported at a molecular level.

Keywords: High-resolution electron microscopy; Structure images; Polyethylene

1. Introduction

High-resolution transmission electron microscopy (HREM) is a powerful tool in investigating the microstructure of solid state by direct imaging. In recent years, the application of HREM to the study of the crystal structure of various materials has become very common. By taking advantage of high-resolution capability of modern transmission electron microscopes (TEM), scientists can directly observe and analyze the crystal structures of materials at an atomic level [1]. However, it is worthy of emphasizing that most of these studies have been carried out on less irradiation sensitive materials such as metals [2] and their oxide compounds [3]. When this powerful tool is applied to the organic materials, especially polymers, the actual challenge occurs due to the destruction of the specimens resulted from the irradiation damage by electron beam. Owing to this reason, the application of TEM to polymers is mainly focused on morphological observations, in which the irradiation damage will not seriously affect the image quality.

Although HREM investigations on polymer crystals are limited by the rapid destruction of the material in the electron beam, it can visualize periodical fine structures at an atomic or molecular level and also sometimes give information on the localized irregular structures such as dislocations. It is proved that the careful use of minimum dose expose techniques as well as particular attention to sample preparation have now made it possible to apply HREM to a number of polymer systems. Consequently, one-dimensional lattice images of a few crystalline polymers have been obtained [4–8], notably isotactic polystyrene [9], poly(*p*-phenylene terephthalamide) [10], and molecular images of poly(*p*-xylylene) single crystal [11].

The present study is concerned with the application of HREM to a relatively irradiation sensitive polymer, polyethylene (PE), whose critical dose is six times less than that of isotatic polystyrene and twenty times less than that of the β form of poly(*p*-xylene) [12]. Simply for this reason, the feasibility of lattice imaging of such a polymer by using HREM has been seriously questioned. Nevertheless, by a more careful TEM operation, for instance, the perfect beam alignment, the strict astigmatism correction, together with an ideal sample preparation, the structure images of single crystal of linear polyethylene were successfully obtained in this work.

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2. Experimental

2.1. Preparation of single crystal of PE

High density polyethylene (HDPE, Jihua Petrochemical Co. china) with an average molecular weight, M_w of 78130, was used. The sample was dissolved at 130 °C in xylene at a concentration of 0.04%. Subsequently, the solution was kept at 70 °C for 20 min and then the self-seeding method [13] was used to grow single crystals. The crystallization was performed at 82 °C. After three days crystallization, the suspension was cooled to room temperature and a droplet was deposited on an electron microscope grid covered with a thin carbon supporting film.

2.2. HREM observation

HREM observation was conducted on a JEOL JEM-2010 TEM with a side goniometer. The accelerating voltage was set to 200 kV. A liquid nitrogen anti-contamination trap and a Gatan image enhancer were also equipped to this machine. The high-resolution pole piece (SHP) with a spherical aberration coefficient (C_S) of 0.5 mm was used. A minimum-dose system was employed with a small beam size (spot size 3) and low beam intensity so as to minimize the irradiation damage of the crystals during examination. The HREM images were recorded on Lekai photographic plates at direct magnifications ranging from 200 000 to 400 000.

2.3. Optical diffraction and image processing

Optical diffraction (OD) and post-possessing of HREM images were performed using a commercial software package, CRISP (Crystallographic Image Processing Software Package, Softhard Technology Inc., Sweden, Ver. 1.3a).

The image was scanned and transferred to a computer using a P800 scanner made in Taiwan and Photo Magic version 1.0 software (Micrografx Inc. USA).

2.4. Resolution limiting factors of electron microscopy

Image formation in TEM can be explained from the standpoint of contrast formation. The contrast formation in TEM can be classified into two types: amplitude contrast and phase contrast. When very thin specimens are observed with a TEM at a fairly high accelerating voltage (>100 kV), the specimens are regarded as phase objects that do not affect the amplitude, but do change the phase of incident electron waves passing through them. Therefore, in a high-resolution study, the phase contrast is very important in the imaging of thin objects. The resolution of an electron microscope is determined by the phase contrast transfer function sin $\chi(\mu)$. Here $\chi(\mu)$ is the phase retardation or the advance of the scattered electron and is expressed as [14],

$$\chi(\mu) = \pi\lambda\Delta f\mu^2 - 0.5\pi C_S\lambda^3\mu^4 \quad (1)$$

where μ is the spatial frequency, λ the electron wave length, C_S the spherical aberration coefficient and Δf the defocus value. In order to obtain an image which reflects the true structure of the specimen, high resolution electron micrograph should be taken under optimum focus conditions (Scherzer focus) determined by sin $\chi(\mu)$. The phase contrast transfer function for 200 kV electrons for a defocus value of 41 nm is shown in Fig. 1. Under this focus the extended region of transfer function near unity is observed. Thus 41 nm under focus is estimated as the optimum defocus for JEM-2010. The reciprocal value of the first zero point in the transfer function ($1/\mu_p = d_p$) is a measure of the optimum resolution of the microscope. Accordingly, the point resolution of the employed TEM is calculated as d_p = 0.197 nm.

3. Results and discussion

Fig. 2(a) shows the typical TEM morphology of single crystals of PE obtained by self-seeding method. The PE lamellar single crystals appear as typically diamond-shaped true lozenges. The insert (Fig. 2(b)) of the same picture gives selected-area electron diffraction of the lamellar crystal. Obviously, the diffraction spots are arranged in a typical PE electron diffraction pattern. By using gold as the calibration standard, the diffraction spots were indexed on the base of an orthorhombic unit cell of PE crystal whose lattice dimensions are $a = 0.7417$ nm, $b = 0.495$ nm, c (chain axis) = 0.2547 nm. As illustrated in Fig. 2(b), the pattern is characterized by very strong (200), strong (110) and ($\bar{1}$10) reflections, corresponding to lattice spacing of 0.37, 0.41 and 0.41 nm, respectively. The diffraction pattern corresponds to a beam direction of ⟨001⟩, giving evidence that the polymer chains in the crystal are oriented perpendicular to the specimen substrate as well as the lamellar surface due to PE chains proved along the direction of c-axis in the orthorhombic crystal structure.

This kind of single crystals of PE were prepared and

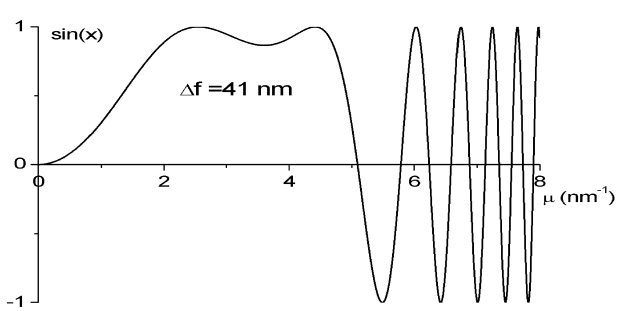
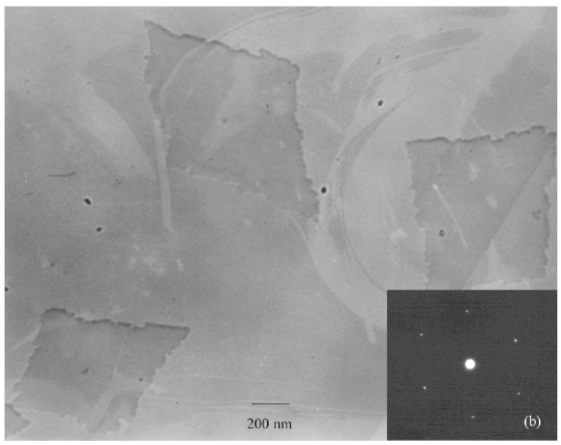


Fig. 1. Phase contrast transfer function for JEM-2010 operated at 200 kV with a defocus of 41 nm (C_s = 0.5 mm). The extended region with amplitude near unity is observed. The expected resolution is about 0.197 nm.

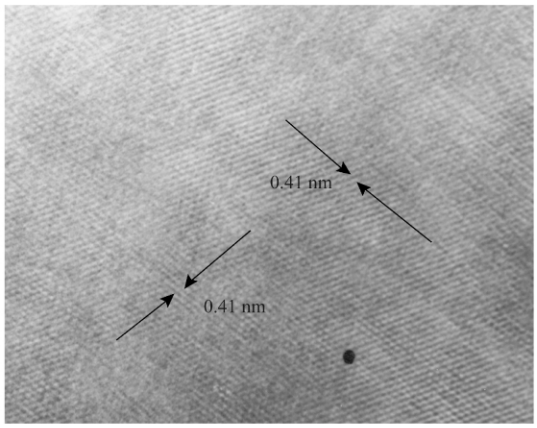


(a)

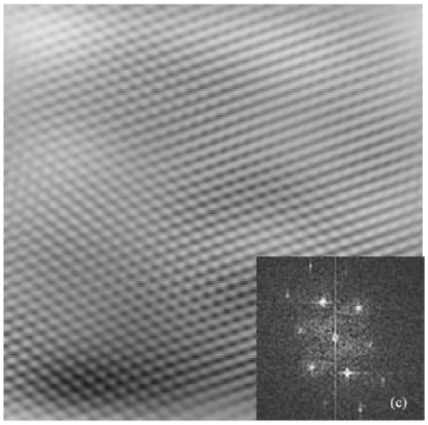
Fig. 2. (a) Bright field TEM morphology of single crystals of polyethylene; (b) the corresponding selected-area electron diffraction.

applied to resolve its structure imaging. Owning to the extreme irradiation sensitivity of PE crystals, special care was taken in TEM operation to avoid serious irradiation damage. Fig. 3(a) shows the obtained high-resolution bright field micrograph of a part of a PE single crystal. This HREM image contains at least two sets of lattice fringes running in different directions and crossing each other in a relatively large area. These two sets of fringes, which can be easily observed in the micrograph, demonstrate very good lattice perfection. Fringes in each set are almost straight and nearly parallel to each other. The spacing between the fringes in both sets was found to be 0.41 ± 0.05 nm, which is close to the *d*-spacing of (110) and ($\bar{1}$10) planes. Since both sets of fringes superpose one another over the most area of the image, it is not likely that these superpositions correspond to two different overlapping grains but rather that they originate from within the same grain. Therefore, the electron beam must be parallel to a certain zone axis of the crystal. That is, one set of fringes comes from (110) planes, and the other corresponds to ($\bar{1}$10) planes. From the HREM image, the angle between these two lattice planes is about 67°, which is in good agreement with the value of 67.5° calculated from the intersection of the (110) and ($\bar{1}$10) planes in the orthorhombic PE unit cell determined by Bunn [15]. Although, only two sets of lattice fringes are observed in the micrograph, lattice fringes corresponding to other planes with much smaller spacing may have been resolved already, but they would not be clear enough to be distinguished in this image with the presence of background noise.

Generally, the quality of HREM images directly recorded on TEM negatives is always suffered from low contrast, radiation sensitivity and noise. In this work, an attempt was made to improve the image by crystallographic image processing using CRISP [16]. Fig. 3(b) and (c) shows reconstructed HREM image and the corresponding OD



(a)



(b)

Fig. 3. (a) High-resolution electron micrograph of single crystal of polyethylene in *a*–*b* projection; (b) the enlarged optically processed image; (c) and its optical diffraction.

pattern from a portion of the HREM image in Fig. 3(a), respectively.

The reconstructed HREM image shown in Fig. 3(b) indicates clearly that the polymeric chain segments are along *c*-axis projected as dots arranged according to the orthorhombic unit cell of polyethylene. Moreover, the OD shown in Fig. 3(c) shares an identical pattern with the electron diffraction of PE single crystal from ⟨001⟩ zone. The same pattern between the electron diffraction from (*hk*0) planes of PE single crystal (Fig. 2(b)) and the OD (Fig. 3(c)) from its high-resolution micrograph (Fig. 3(a)) indicates that the micrograph sufficiently reflects the crystal structure of PE single crystal. On the other hand, the position of each molecular chain segment is precisely localized. Furthermore, the presence of dislocation in the crystal should be detectable through a careful analysis of the original HREM image. This work is in progress and will be presented subsequently.

The HREM image of the edge of another PE single crystal shown in Fig. 4(a) also demonstrates a two-dimensional periodic structure, with the wide-spaced fringes prevailing over the most area of the crystal, in which no disorder can be distinguished along the fringes. The spacing of these wide lattice fringes was measured directly from the image to be 0.41 ± 0.05 nm, which corresponds to the $(1\bar{1}0)$ planes (0.411 nm). The other lattice fringes with a spacing of 0.22 ± 0.05 nm, which are relatively faint in contrast and narrow in spacing, make an angle of about 83° with the $(1\bar{1}0)$ fringes. Correspondingly, these narrow lattice fringes belong to (310) planes. Fig. 4(b) and (c) shows the HREM image after computer processing and the corresponding OD pattern, respectively. The OD pattern also gives some higher order reflections.

4. Conclusion

In summary, we have successfully demonstrated the structure images of PE single crystal by utilizing HREM, although PE crystal is so sensitive to radiation damage. Two different two-dimensional lattice fringes were resolved. The images were obtained using the ⟨001⟩ incident electron beam direction. The success of imaging the (*hk*0) lattice planes of PE single crystal is assumed to be the contribution of using a higher accelerating voltage and a substantial technique in TEM operation. Based on the knowledge and experience accumulated in this work, we are confident that this powerful tool can be further applied to other polymers with a similar or even lower critical dose of irradiation damage compared to that of PE. In particular, it is intended to use the technique to study the structure defects such as

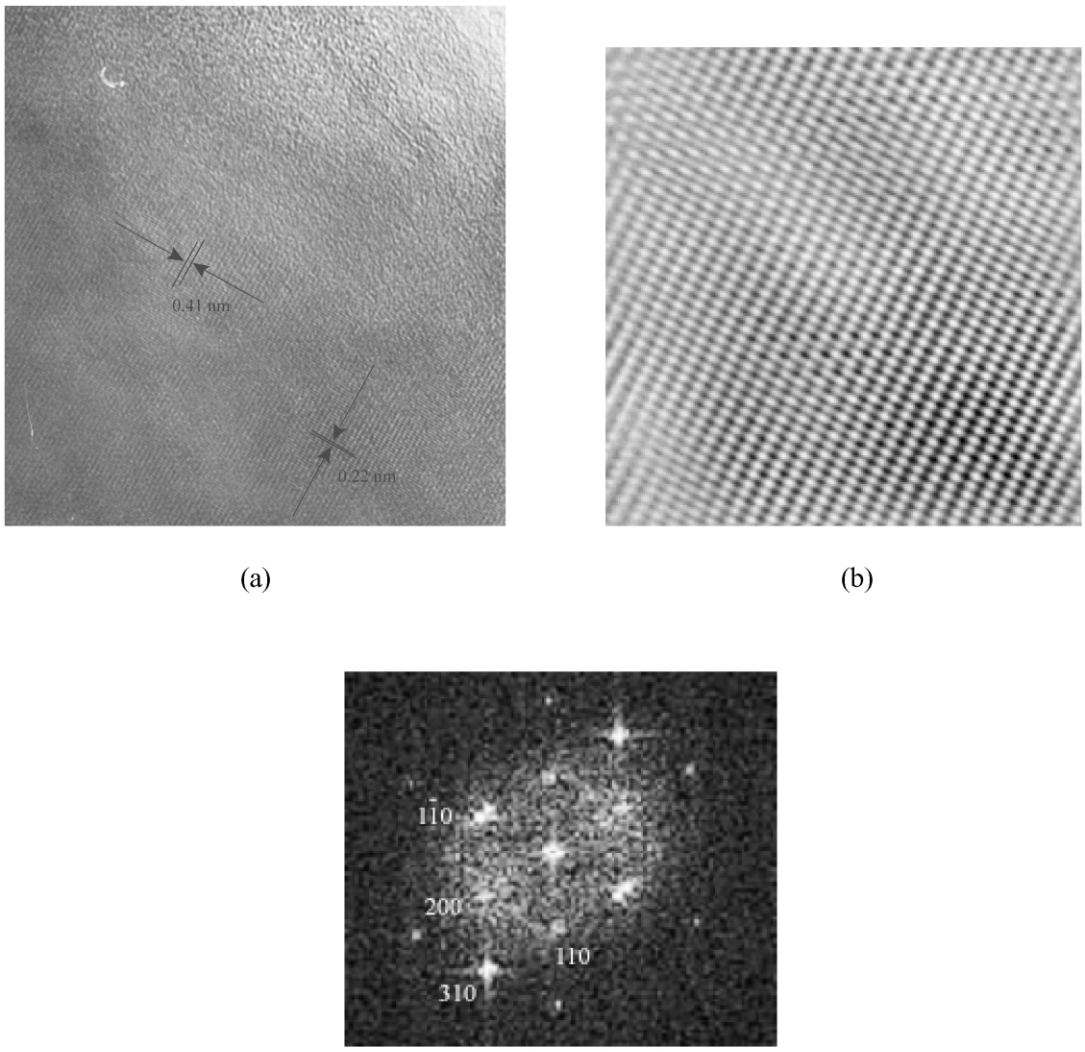


Fig. 4. (a) High-resolution electron micrograph of the edge of PE single crystal in *a*–*b* projection; (b) its enlarged optically processed image; (c) and the corresponding optical diffraction.

dislocations, stacking faults, grain boundaries and twins in these materials.

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