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High resolution electron microscopy study of single chain single crystals of gutta percha

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Single chain single crystals (SCSC) of gutta percha (GP) were prepared by a dilute-solution spraying method. Electron diffraction (ED) patterns revealed that the single chain single crystal was of a new crystalline modification, the δ form. The images of SCSC of GP obtained with a high resolution electron microscope (HREM) showed a two dimensional periodic structure. Most of the images consisted of lattice fringes derived from the $\langle 001 \rangle$ zone. This is the first time that the single chain single crystal images of GP have been observed at a molecular level. Micrographs were image processed using optical filtering methods to improve the signal-to-noise ratio, and were compared with computer-generated simulations of the images. From the viewpoint of the defects seen in high resolution images, the crystal formation and melting processes are discussed. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: single-chain single crystal; gutta percha; high resolution electron microscopy)

INTRODUCTION

The single chain single crystal consists of only one macromolecule, a case unique to polymers. Single chain single crystals of polyethylene oxide (PEO)[1] isotactic polystyrene (PS)[2], cis-1,4-polybutadiene (PBD)[3] and *trans*-1,4-polyisoprene (gutta-percha, (GP))[4,5] have been obtained in recent years, promoting the study of SCSC of polymers and polymer crystallography. Despite the morphological and preparational investigations mentioned above, no study has yet been reported in the literature on the arrangement of the molecular unit in the SCSC. The SCSC of GP has been prepared and investigated by us and a new crystalline modification has been found[4,5]. In this paper, the crystal structure of the new modification of SCSC of GP will be described at the molecular level by using high resolution electron microscopy.

A high resolution transmission electron microscope is a powerful tool for studying the microstructural solid state by direct imaging. It is therefore widely used in structural studies of metals and semiconductors owing to their ability to withstand electron irradiation. It is, however, difficult to apply this method to polymer crystals because of their sensitivity to electron-beam irradiation. Despite this, by using a JEOL 200EXII HRTEM equipped with a Gatan image intensifier and a liquid nitrogen finger, some satisfactory results have been obtained from the study of SCSC of GP.

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EXPERIMENTAL

Preparation of SCSC of GP

Natural gutta percha was fractionated by precipitation from toluene solution into methanol in the usual way, and the fraction of $[\eta] = 8.17$ g/dL, $M = 3.73 \times 10^6$ was dissolved in chloroform to make a 5×10^{-3} wt% solution. A carbon film on a Cu grid was placed on a filter paper which had been fully wetted with the correct amount of ethanol. The GP solution was then atomizer sprayed onto the carbon film on the Cu grid. After evaporation of the solvent, SCSC were deposited on the grid.

HREM observation

A JEOL-200EXII high resolution transmission electron microscope with a top-entry goniometer was used in this work. A nitrogen cooling finger and a Gatan image enhancer were also fitted. The accelerating voltage was set to 200 kV. The high resolution pole piece (SHP) used here had a spherical aberration coefficient (Cs) of 0.7 mm. An objective aperture of 50 μm and a field limiting aperture of 100 μm were selected. A minimum dose system (MDS) was used in the image-recording process in order to minimize the radiation damage. The HREM images were recorded on Gongyuan photographic plates at direct magnifications ranging from 200 000 to 400 000.

Optical diffraction and image processing

Optical diffraction (OD) and image processing were performed using the Crisp version 1.3a crystallographic image processing software package (Softhard Technology Inc. Sweden).

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

Computer simulation

Computer simulation was performed on an Indigo workstation using the software package Cerius^2 version 1.6 (Molecular Simulations Incorporated (MSI), USA).

RESULTS AND DISCUSSION

Morphology and electron diffraction of SCSC of GP

Figure 1 shows the morphology and electron diffraction pattern of some crystallized particles of gutta percha. The obtained particles were confirmed to be single chain particles by the Pt shadowing method[6]. The average diameter of the particles was 20 nm, from the shadowing angle and the shade length, the height of the particle was determined to be 20 nm. If the single-chain particles are assumed to have the same density as the bulk crystals, 1.05 g/cm^3, the average molar mass of the observed particle is 3.97×10^6, which is in agreement with the known molecular weight of 3.73×10^6 confirming that the obtained particles are single-chain particles. The shadowing process and photograph were described in detail in our previous publication[4].

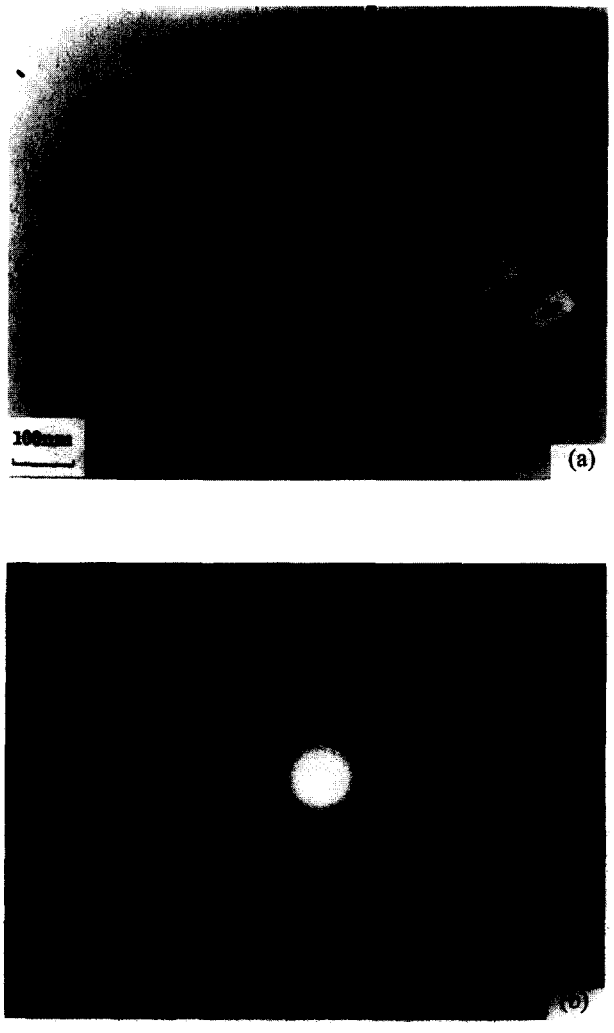


Figure 1 Morphology of single chain single crystals of gutta percha (a) and the corresponding electron diffraction pattern of the two marked particles (b)

Figure 1b shows the selected-area electron diffraction pattern of the marked two single-chain single crystals in *Figure 1a*. The ED pattern indicates that both particles are single crystals having the same crystal structure with different orientation. The diffraction spots form a regular hexagonal form. By using gold as the calibration standard, we found a Bragg spacing of 0.602 nm for the nearest diffraction spots from the electron beam centre, and Bragg spacings of 0.354 nm and 0.301 nm for next nearest diffraction spots from the electron beam centre. The diffraction pattern shows that the crystal is of a new crystalline modification, the δ form. The crystal structure and molecular conformation of the δ crystalline modification of gutta percha have been determined in a previous paper[5]. The unit cell constants of the δ crystalline modification of GP are: $a = b = 0.695$ nm, $\alpha = \beta = 90°$, $\gamma = 120°$, the space group is P6. The common ED shown in *Figure 1b* is the ED along the $< 001 >$ zone of the crystal.

HREM image

Figures 2–4 show the HREM images of different single chain single crystals. *Figure 2* shows the HREM image of a particle under 3000 × magnification. The particle size is about 20 nm, corresponding to a single chain single crystal. This SCSC has regular edges and corners and shows two dimensional periodic structure. The *d*-spacings along two directions are both 0.60 nm; the angle between the two lattice planes is 60°; the *d*-spacing and the angle between the two lattice planes are in accord with the findings of the electron diffraction patterns shown in *Figure 2b*.

The experimental images are always affected by low contrast, radiation sensitivity and noise. In this work, an attempt was made to improve the image by crystallographic image processing using CRISP[7]. *Figure 2c* and *Figure 2d* show the HREM image after computer processing and the corresponding optical diffraction pattern of the HREM image in *Figure 2a*, respectively. From *Figure 2c* it can be seen that there are some defects inside the crystal; however, the defects do not affect the whole regularity of the crystal, and a very good electron diffractogram is still obtained.

Figure 3 is the HREM image of a SCSC of gutta percha of a nearly tetragonal shape. While most of the crystal has the same structure as the SCSC in *Figure 2a*, it shows more interesting microstructure, in that at the two edges of the crystal, a new periodic structure with a *d*-spacing of 0.35 nm has emerged, which can be indexed (110). The appearance of the new crystalline plane is caused by orientation.

Figure 4 shows the HREM image of another SCSC under 1500 × magnification. Although this SCSC is not of regular shape, it shows the two-dimensional image clearly. It is about 15 nm in size, in accordance with the size of single chain particles for this material. From the HREM image, the following details could be seen: (1) both *d*-spacings along the two directions are 0.600 nm; (2) the angle between the two lattice planes is 60°; (3) there is a defect in the middle of this crystal; (4) the crystal is an entire crystal, there is no boundary inside the crystal. The *d* spacing is in good accordance with the results of the ED pattern shown in *Figure 1b*. From the *d*-spacing and the angle between the lattice plane, this SCSC of GP should have the same ED pattern as *Figure 1b*, which is indeed the case as proved by the optical diffractogram in *Figure 4b*.

Figure 4c is the enlarged and computer processed HREM image of *Figure 4a*. It can be seen that the crystal has an angle of about 120° in the left-hand corner in *Figure 4c*; there is no

obvious boundary and angle in the right hand corner, probably caused by a crystal which has not grown large enough because the length of the molecular chain is too short.

The defect in the SCSC of *Figure 4a* and *Figure 4c* is very significant. The defect may be due to the fact that the thickness of the crystal in the defect region is very thin. The molecular chain in a SCSC is necessarily folded. In the defect region the stem length of folded segments may be shorter than that in other regions inside the crystal. It could be inferred that the defects under high magnification would look like holes under low magnification. In fact, such a phenomenon was seen in the case of SCSC of polybutadiene (PBD). The discovery of defects in HREM images could give a good explanation for the fact that despite the morphology of SCSC of PBD having some holes, a typical ED of a single crystal was still obtained[3].

From above HREM images, it can be concluded that single-chain crystals have periodic structures on the molecular level whether they have regular crystalline contours or not.

HREM image simulation

It was confirmed from the ED pattern[5] that the SCSC of GP is a δ crystalline modification. The unit cell constants and molecular conformation were determined by computer simulation and experimental ED. A reasonable crystal structure was built.

The diffraction pattern from GP, the HREM image of which is shown in *Figure 2*, indicated a $< 001 >$ zonal projection. The simulated model structure calculated from the diffraction pattern in this projection is shown in *Figure 5*. The coordinates of all the atoms in the unit cell were then used to calculate the corresponding HREM image as shown in *Figure 6a*. The calculated image was for a sample thickness of 20 nm, the defocus value was $-$ 100 nm. Compared with the experimentally observed images shown in *Figures 2–5*, it is clear that the experimental images

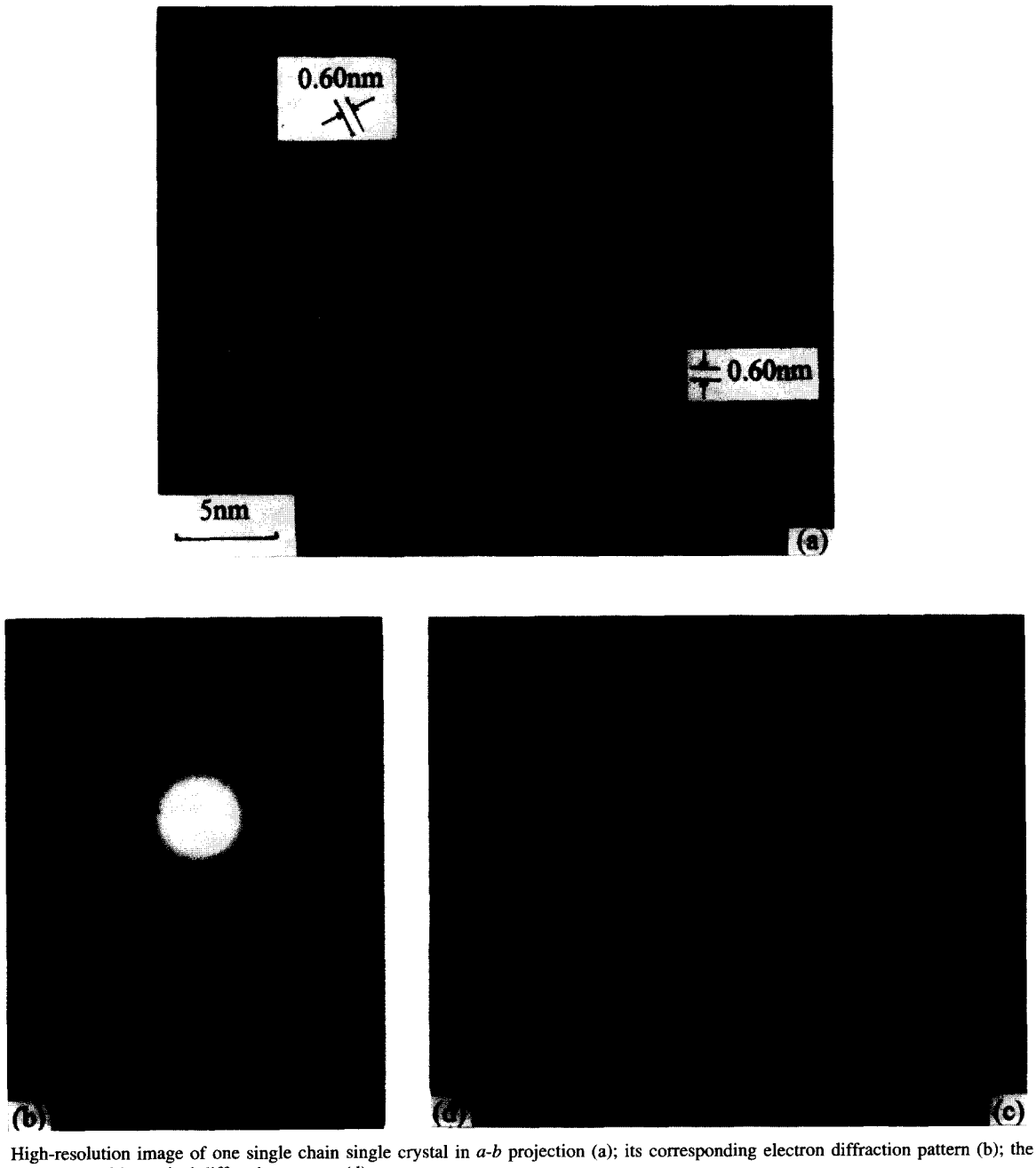


Figure 2 High-resolution image of one single chain single crystal in *a-b* projection (a); its corresponding electron diffraction pattern (b); the optically-processed image (c); and its optical diffraction pattern (d)

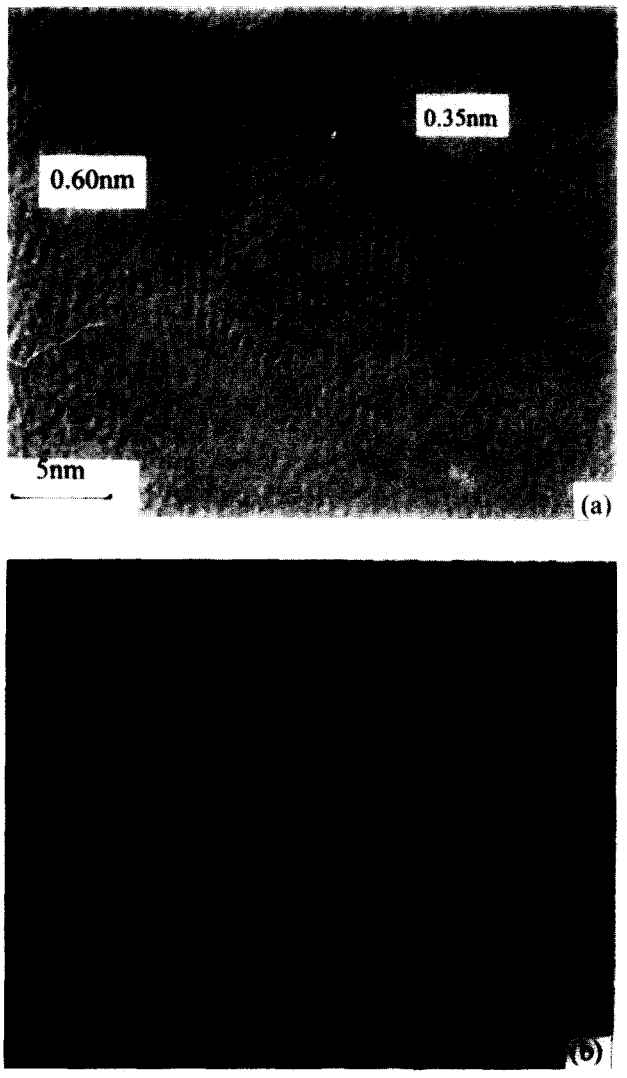


Figure 3 High-resolution image of one single chain single crystal (a) and its enlarged optically-processed image (b)

agree well with the calculated image. These results therefore prove that the structure obtained from the analysis of the electron diffraction patterns and the molecular model shown in *Figure 5* are correct.

The process from crystalline to amorphous particle of SCSC

Figure 7a and *Figure 7b* show the HREM images of the same SCSC of GP at different times. The size of this SCSC is about 10 nm. Its one dimensional HREM image was recorded. During the imaging process, the crystallinity of the crystal decreased due to the damaging effect of the electron beam irradiation. Comparing *Figure 7b* with *Figure 7a*, it is clear that the crystal began to become amorphous starting from the edges of the crystal. Meanwhile, it was observed that the crystalline lattice inside the crystal gradually disappeared. Thus HREM images can actually reveal the melting process from crystalline to amorphous state on the molecular level.

CONCLUSION

Electron diffraction patterns and HREM images of single chain single crystals of gutta percha were examined. The Bragg spacing from ED and HREM images are in good accord.

It is worthwhile recapitulating what we have learned from the observation of HREM images of the SCSC of GP: (1) there is a defect region in the crystal showing a vague lattice image, (2) the defect does not affect the coherence of the whole crystal lattice. It may be inferred that very probably the crystalline stem length is much shorter in the defect region leading to different contrast in the HREM image. As the solvent evaporates quickly, the molecule crystallizes quickly, so the irregular folding of the single chain exists before crystallization starts. The crystallization of the folded single chain must proceed by lateral aggregation of the chain as hexagonal close packing, with some readjustment of crystalline stem length. It is natural that in some regions short crystalline stem lengths remained because of hindrance of chain movement. As the HREM image of the SCSC of GP is the projection of

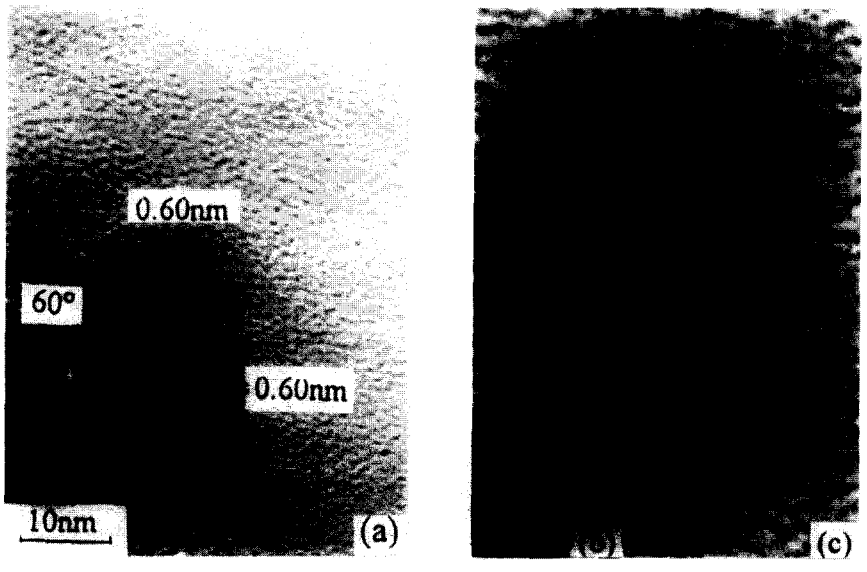


Figure 4 High-resolution image of one single chain single crystal (a); its corresponding optical diffraction pattern (b) and enlarged optically-processed image (c)

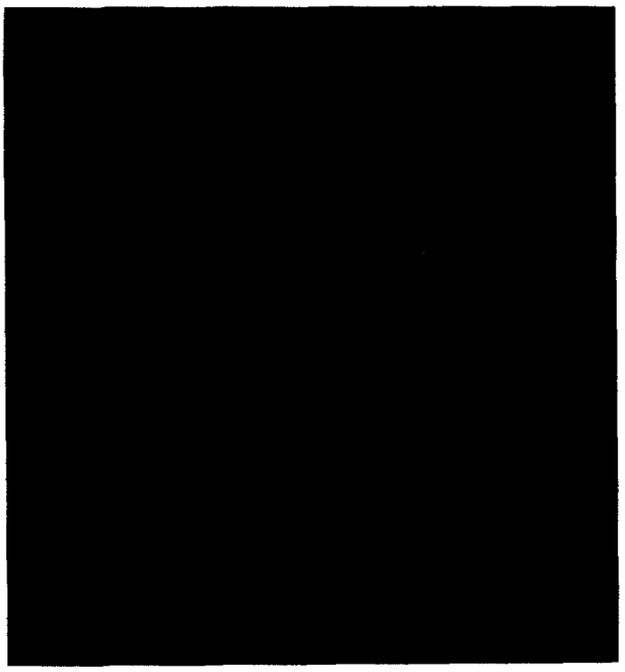


Figure 5 Projection of the δ-modification of the single chain single crystal of gutta percha along the < 001 > zone

the crystal lattice along the chain direction, the difference in stem lengths leads to the uneven density of the structural projection and therefore to the region of short stem lengths emerging as a defect in the HREM images.

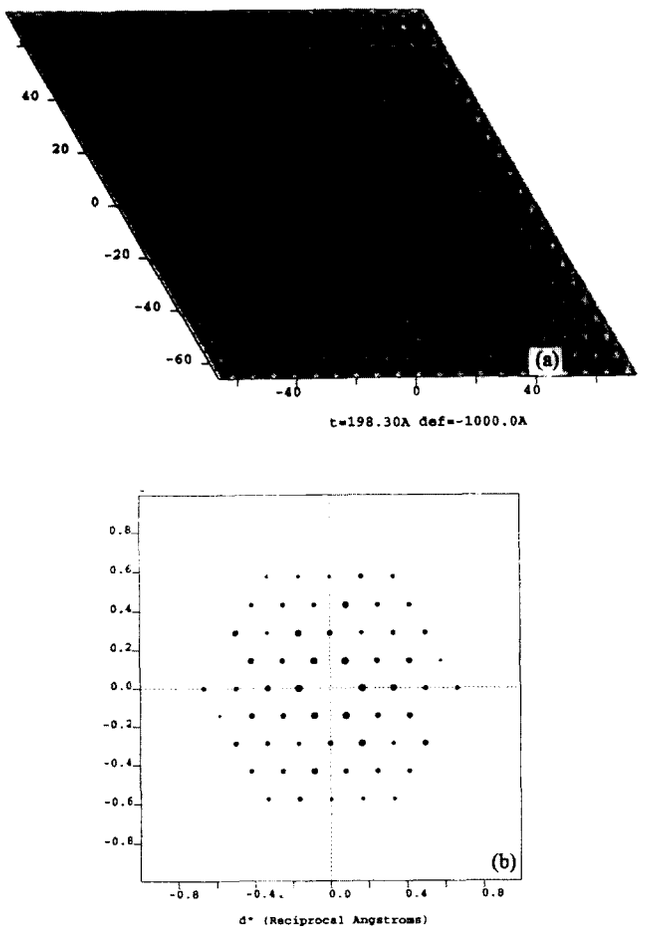
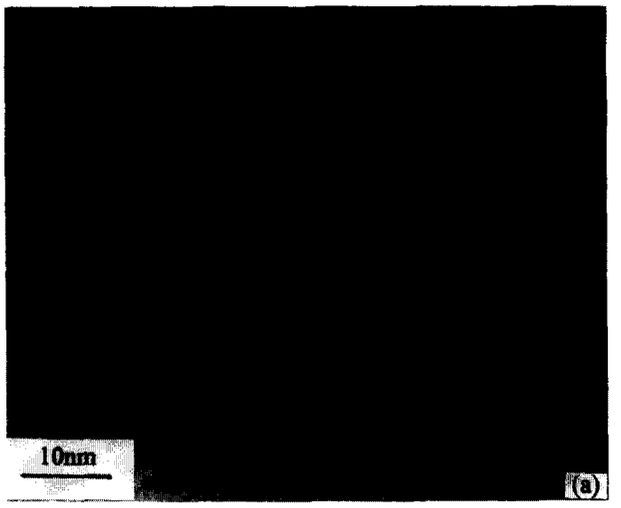


Figure 6 Computer-simulated high resolution image (a) and electron diffraction pattern (b) of the δ-modification of the single chain single crystal of gutta percha along < 001 > zone



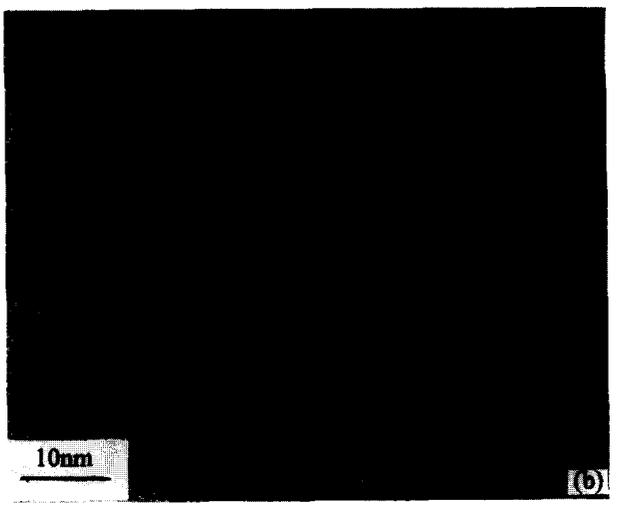


Figure 7 The melting process of the single chain single crystal of gutta percha revealed by high resolution imaging

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