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A new crystal modification of gutta percha

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Single chain and pauci chain single crystals of gutta percha in nanometer size were prepared by a dilute solution spraying method. A new crystal modification of gutta percha was found. The unit cell of the new modification of gutta percha was determined by electron diffraction crystal structure analysis to be a hexagonal form with cell dimensions: $a = b = 0.695$ nm, $c = 0.661$ nm, $\alpha = \beta = 90°$, $\gamma = 120°$; the space group is P6. The molecular packing in the unit cell was determined by computer modelling with Cerius^2 2.0 software. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: gutta percha; single chain single crystal; pauci chain single crystal)

INTRODUCTION

The study of single chain single crystals (SCSCs) and pauci chain single crystals (PCSCs) of polymers is a new research field in polymer crystallography[1–3]. The study of the crystalline characteristics of a single macromolecular chain could offer the necessary structural data to elucidate many important problems in addition to the intermolecular and intramolecular interactions, such as the morphology before and after crystallization, the crystallization process, the crystal structure and the interfacial structure between crystalline and amorphous regions. So the study of single chain single crystals of polymers is an exciting topic. The preparation, morphology and structure of the SCSCs of cis-1,4-polybutadiene (PBD)[3] and gutta percha (GP)[4] have been described previously. It was found that the SCSCs tend to give a hexagonal shaped electron diffraction (ED) pattern, and the ED pattern could not be indexed with the known crystal structures of PBD and GP respectively. This implied that new crystalline modifications are involved in the SCSCs of PBD and GP.

Gutta percha (trans-1,4-polyisoprene) is a natural crystalline polymer. Its crystalline character has been investigated by many scientists. According to Fischer[5], gutta percha can form three kinds of crystal structures, the α-, β- and γ-forms under different conditions. The α- and γ-type crystals belong to the monoclinic form, while the β-type belongs to the orthorhombic form. In this paper, a fourth crystalline modification of GP, found in nanometer size single crystals of GP, was studied in detail.

EXPERIMENTAL

Specimen preparation

Fallen leaves of *Eucommia Ulmoides* were powdered and extracted with acetone to remove resins. Then, gutta percha (GP) was extracted from these powdered leaves with toluene and precipitated by acetone. The extraction and precipitation were repeated several times to yield the GP sample. The GP sample was fractionated by precipitation from toluene solution into methanol in the usual way; the fraction of $[\eta] = 8.17$ dL/g was dissolved in chloroform to make a 5×10^{-3} wt% solution. The solution was atomizer sprayed onto a carbon film on a Cu grid. The carbon film on the grid was put onto a filter paper which had been fully wetted by dropping a proper amount of ethanol on it before the GP solution was sprayed. After evaporation of the solvent, SCSCs were deposited on the grid.

Electron microscopy

In order to minimize the damage or even melting of the single crystals of GP on the carbon film during electron microscopy (EM) and electron diffraction (ED) study, the morphology observation and ED were carried out at 173 K. The transmission electron microscope used was a Hitachi H-500 with a low temperature attachment under liquid nitrogen cooling. The temperature of the specimen stage was continuously adjustable from 123 K to room temperature.

The tilting series electron diffraction was obtained by using a JEOL 2010 electron microscope with a goniometer stage. A 613-DH tilt holder was used to obtain different crystallographic projections of the unit cell. The tilt angle was adjusted until new zones appeared. The maximum tilting angle could reach $\pm 30°$.

Computer modelling

Computer modelling was performed on an Indigo workstation; the Cerius^2 2.0 package produced by Molecular Simulations Inc., USA was used.

RESULTS AND DISCUSSION

Morphology and structure of SCSCs of GP

The preparation of SCSCs of GP has been described previously[4]. The GP sample was dissolved in chloroform to

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make a very dilute solution, and then a glass atomizer was used to spray the GP solution onto a carbon film on a Cu grid. Because the solution was very dilute, each solution droplet sprayed contained only one or no molecules, so a single chain single crystal could form after solvent evaporation at room temperature. In order to control the crystallization process of SCSCs, the carbon film was put onto a filter paper which had been fully wetted by dropping a proper amount of ethanol (precipitant of GP) onto it before the GP solution was sprayed. Ethanol on the filter paper could permeate the carbon film so that actually the GP solution was sprayed onto a non-solvent coated surface. Trials showed that the amount of ethanol on the filter paper had important consequences during crystallization of the single-chain GP particles on the carbon film; it could affect the morphology and structure of SCSCs of GP. When the amount of ethanol is large, the SCSCs of GP are irregular shaped and of β-modification inferred from electron diffraction. When the amount of ethanol is appropriate, the SCSCs of GP are polygonal shaped, and their electron diffraction patterns are of hexagonal symmetry which could not be indexed by the known crystalline structures of GP.

Figure 1 shows the morphology and electron diffraction pattern of a SCSC of GP. This SCSC is hexagonal shaped, about 20 nm in its lateral size (*Figure 1a*), and it was confirmed to be a single chain particle by a Pt shadowing method[6]. From the shadowing angle and the shadow length, the height of the particle was determined to be 20 nm. If the single chain particle is assumed to have the same density as the bulk crystals, 1.05 g/cm^3, the molar mass of the observed particle is 3.97×10^6, in agreement with the measured molar mass 3.73×10^6, so that the particle is a single chain particle. The ED pattern of this SCSC is shown in *Figure 1b*. The diffraction spots form a regular hexagonal point lattice, with a Bragg spacing of 0.602 nm by using

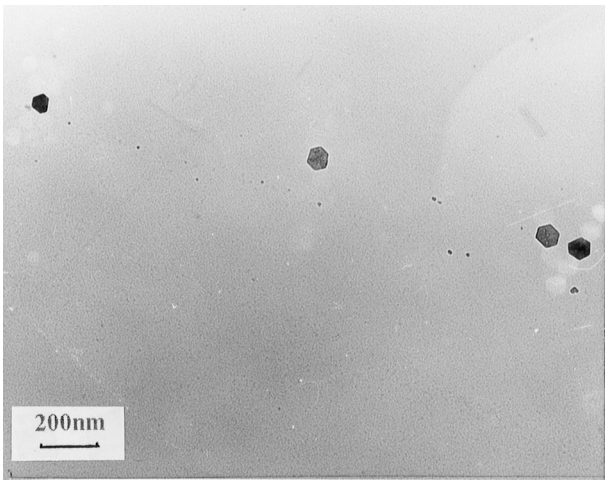

Figure 2 Morphology of pauci chain single crystals of gutta percha

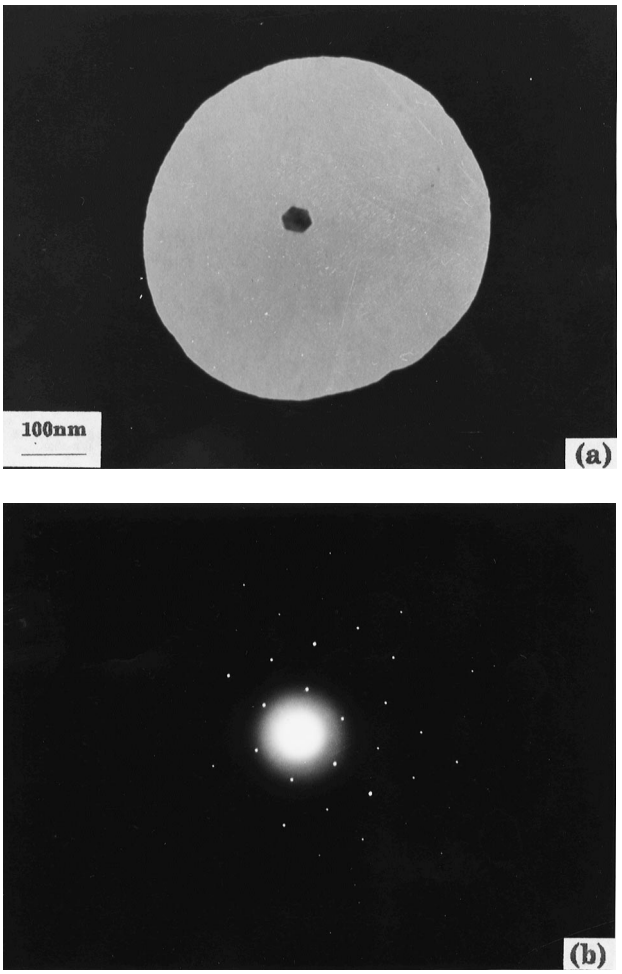

Figure 1 Morphology of one single chain single crystal of gutta percha (a) and its corresponding electron diffraction pattern (b)

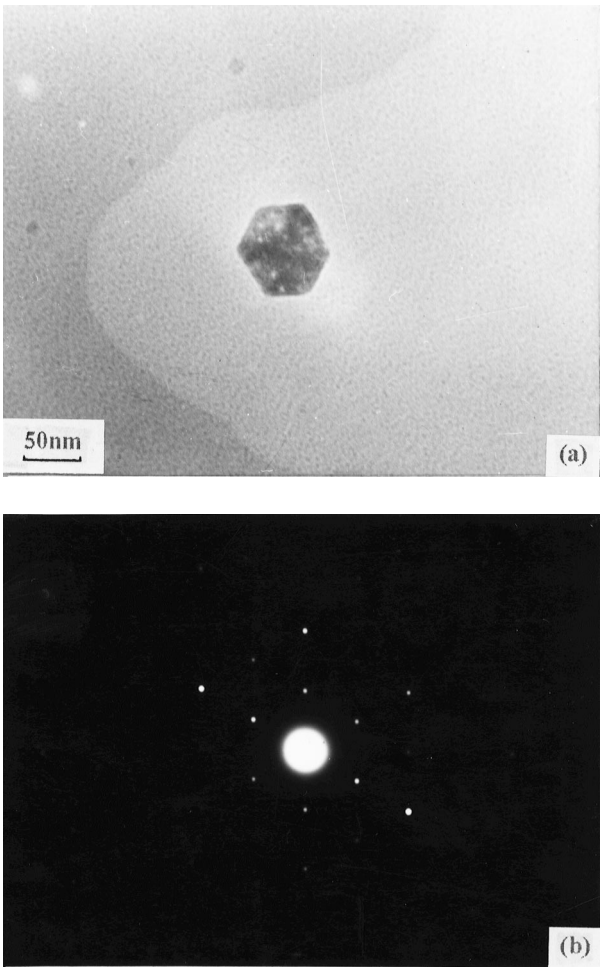

Figure 3 Morphology of one pauci chain single crystal of gutta percha (a) and its corresponding electron diffraction pattern (b)

gold as the inner standard. The next nearest diffraction spots from the electron beam centre show Bragg spacings of 0.354 and 0.301 nm. Thus the diffraction pattern shows that the crystal is neither of the α-modification nor of the β- or γ-modifications. It is a new crystalline modification.

Pauci-chain single crystals of GP

Owing to its very small size, it is difficult to perform crystal structure analysis of a SCSC. So pauci-chain single crystals (PCSCs) of GP are prepared under the same conditions as for SCSCs. A PCSC is a single crystal which contains several to dozens of chains of particles. *Figure 2* shows the morphology of several PCSCs and some SCSCs of GP. Big and small crystals coexist in the photograph. The hexagonal shaped big crystals are PCSCs; their average lateral size is about 80 nm. There are some irregular shaped small crystals near the PCSCs. The lateral size of these small crystals is about 20 nm; they are SCSCs. The Pt shadowing results show that the height of a PCSC is nearly the same as that of a SCSC, so that each PCSC contains ca. 16 molecules.

Figure 3 shows the morphology of one PCSC and its corresponding electron diffraction pattern. The crystal in *Figure 3a* is hexagonal shaped, the distance between the three parallel surfaces of the hexagonal profile of the single crystal is 80 nm, and the angle between the adjacent two edges is 120°. The electron diffraction spots in *Figure 3b* are of hexagonal symmetry. By using gold as the inner standard, the innermost six spots correspond to a Bragg spacing of 0.602 nm, and the next nearest diffraction spots from the electron beam centre show Bragg spacings of 0.354 and 0.301 nm. The ED results are in accord with that of a SCSC.

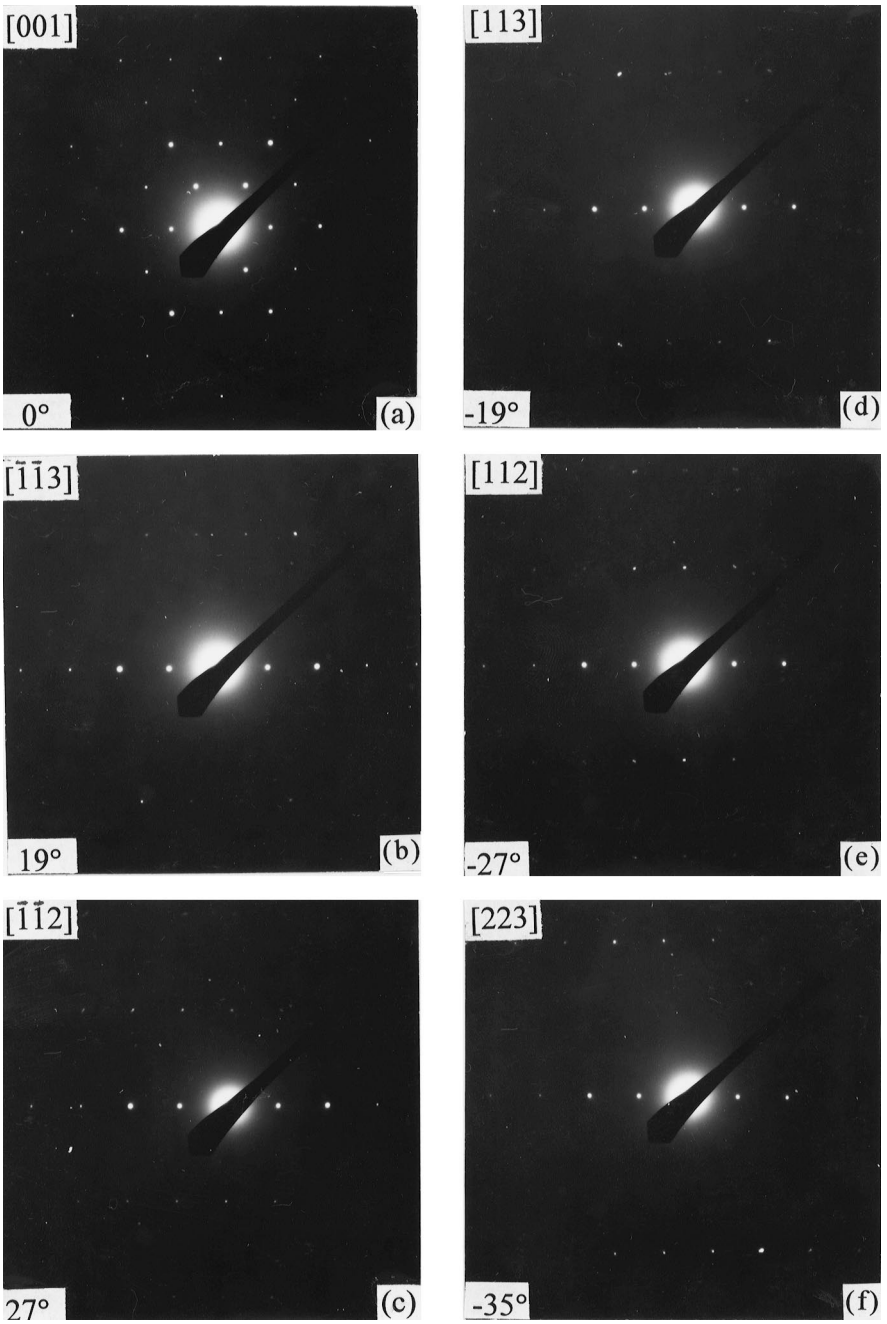

Figure 4 Tilt series of ED patterns of pauci chain single crystals of gutta percha around a^* (tilt angle indicated in lower left-hand corner and corresponding zone in upper left-hand corner)

Table 1 Structure data of gutta percha

Crystalline form	Crystalline modification	Unit cell constants	Ref.
α-form	Monoclinic	$a = 0.798$ nm;	
high melting		$b = 0.629$ nm;	[11]
phase (HMF)		$c = 0.877$ nm; $\beta = 102.0°$	
β-form	Orthorhombic	$a = 0.778$ nm;	
low melting		$b = 1.178$ nm;	[5]
phase (LMF)		$c = 0.472$ nm; $\alpha = \beta = \gamma = 90°$	
γ-form	Monoclinic	$a = 0.59$ nm;	
		$b = 0.92$ nm;	[5]
		$c = 0.79$ nm; $\beta = 94.0°$	
δ-form—a new	Hexagonal	$a = b = 0.695$ nm;	
modification		$c = 0.661$ nm;	This work
		$\alpha = \beta = 90°$, $\gamma = 120°$	

So, it can be inferred that the SCSC and the PCSC prepared in the same conditions have the same crystal form, and this is a new form which is different from the known crystal forms of GP. Let us name the new form as the δ-form of GP.

Crystal structure of the δ-form of GP

Usually, a new crystal structure could be analyzed by X-ray crystallography using a direct phase method[7]. But for polymer single crystals, it is extremely difficult or even impossible to obtain the large single crystal necessary for X-ray structural analysis. Especially for nanometer size SCSCs and PCSCs of polymers, X-ray structural analysis is no longer useful. However, single-crystal diffraction patterns can be obtained from microcrystals by electron diffraction. This may then be the only experimental method available to obtain the desired information about molecular conformation and crystal structure[8–10].

The electron diffraction crystal structure analysis is composed of the simultaneous observation of selected area electron diffraction and micro-crystal tilting. First, the axis, where the most diffraction spots are, is selected as the tilting axis. Then the specimen is tilted around the axis until a new ED pattern appears. Thus various sections of the reciprocal lattice may be obtained. Finally, a reasonable unit cell can be constructed according to the reciprocal lattice and the tilting angle.

*Figure 1*b shows the usually observed ED of the δ-form single crystal of gutta percha. The innermost six diffraction spots are of equal intensity and the spots have a six fold symmetry axis. This demonstrates that there is a hexagonal axis which is perpendicular to the substrate. In order to obtain the structure information in all three dimensions, the tilting method is used. The horizontal axis, a^*, is selected as the tilting axis.

Figure 4 shows a series of ED patterns obtained on tilting a PCSC of GP about the a^* axis. *Figure 4*a is the initial ED pattern; new zones appear at $\pm 19°$, $\pm 27°$ and $-35°$. A $+35°$ tilt was not reached due to constraints by the tilt holder. The diffraction patterns obtained by $\pm$-tilts were identical.

According to the tilting angles and the corresponding reciprocal lattice, the unit cell constants are calculated and given in *Table 1*. The space group is determined to be P6 according to the extinction results. Then, the ED pattern can be indexed, and the initial ED was determined to be the reciprocal lattice along the $\langle 0\ 0\ 1 \rangle$ zone.

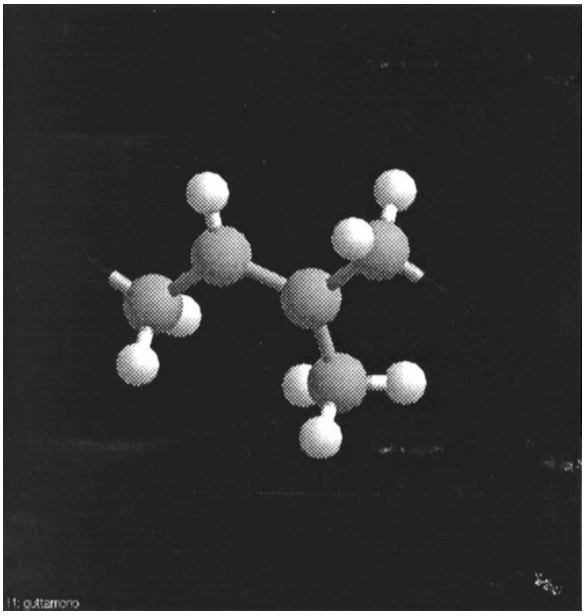

Figure 5 A monomer unit of gutta percha

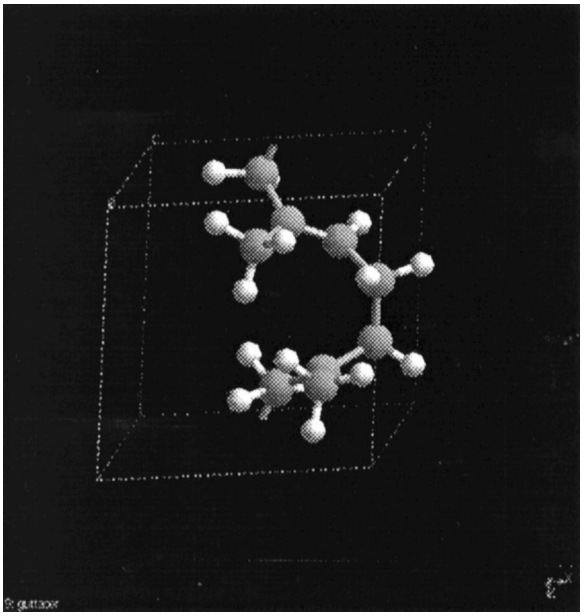

Figure 6 Molecular packing of δ-modification gutta percha in one unit cell

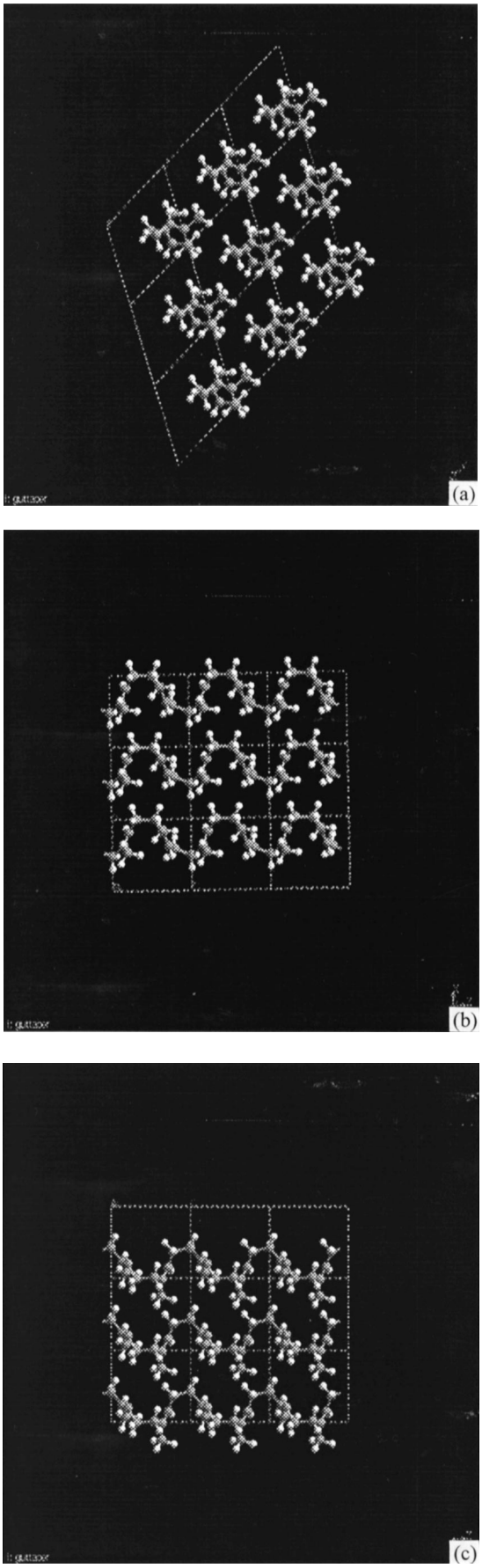

Figure 7 Projections of the crystal structure of δ-modification gutta percha along the following zones (a) ⟨0 0 1⟩; (b) ⟨0 1 0⟩; (c) ⟨1 0 0⟩

Molecular simulation

The molecular arrangement in the unit cell is usually determined by single crystal X-ray diffraction. But GP crystallizes as the δ-form only when the crystal is very small. The traditional X-ray diffraction intensity analysis is not applicable. In this paper, the crystal structure has been determined by electron diffraction. Simulation of experimental electron diffraction patterns in all zones using Cerius[2] software enables the molecular packing to be derived[12].

First, the monomer unit of gutta percha is constructed by using Crystal Building of Cerius[2] (*Figure 5*). Then, the monomer unit is put into the unit cell which has been determined by tilting ED. According to the calculated density, which must be close to one for organic materials, there are two monomer units in one unit cell. The two monomer units constitute a segment in the unit cell. Energy minimizing is used to minimize the crystal energy. When this segment is helical, the crystal energy reaches a minimum. The molecular packing in one unit cell is shown in *Figure 6*.

In principle, the molecule is placed into the unit cell using Cerius[2] software such that the required symmetry of both molecule and unit cell are satisfied agreeing with the observed extinctions and symmetry. The major features of the simulated diffraction pattern should agree with the experimental ones in all zones. Frequently it is necessary to make conformation adjustments to improve the individual intensities, keeping the required symmetry condition satisfied.

Finally, a polymer model structure giving good agreement between calculated and experimental diffraction patterns in all projections is obtained as shown in *Figure 7* showing the polymer crystal structure of a $3 \times 3 \times 3$ unit cell.

By using Cerius[2], the simulated ED patterns could be obtained. *Figures 8a–f*, show the simulated diffraction patterns for all the zones obtained experimentally, and clearly demonstrate good agreement with those shown in *Figure 4*. Extremely good agreement between the experimental and simulated electron diffraction patterns was obtained in all 6 zones for the molecular conformation and packing indicated in *Figure 7*.

CONCLUSION

In this work, a new crystal modification named the δ-modification of gutta percha is found in the case of nanometer size SCSCs and PCSCs. The crystal structure of the δ-modification gutta percha has been determined by tilting electron diffraction and computer simulation. The unit cell has the following constants: $a = b = 0.695$ nm, $c = 0.661$ nm, $\alpha = \beta = 90°$, $\gamma = 120°$; the space group is P6. There are two molecules in one unit cell. The molecular chain is perpendicular to the substrate.

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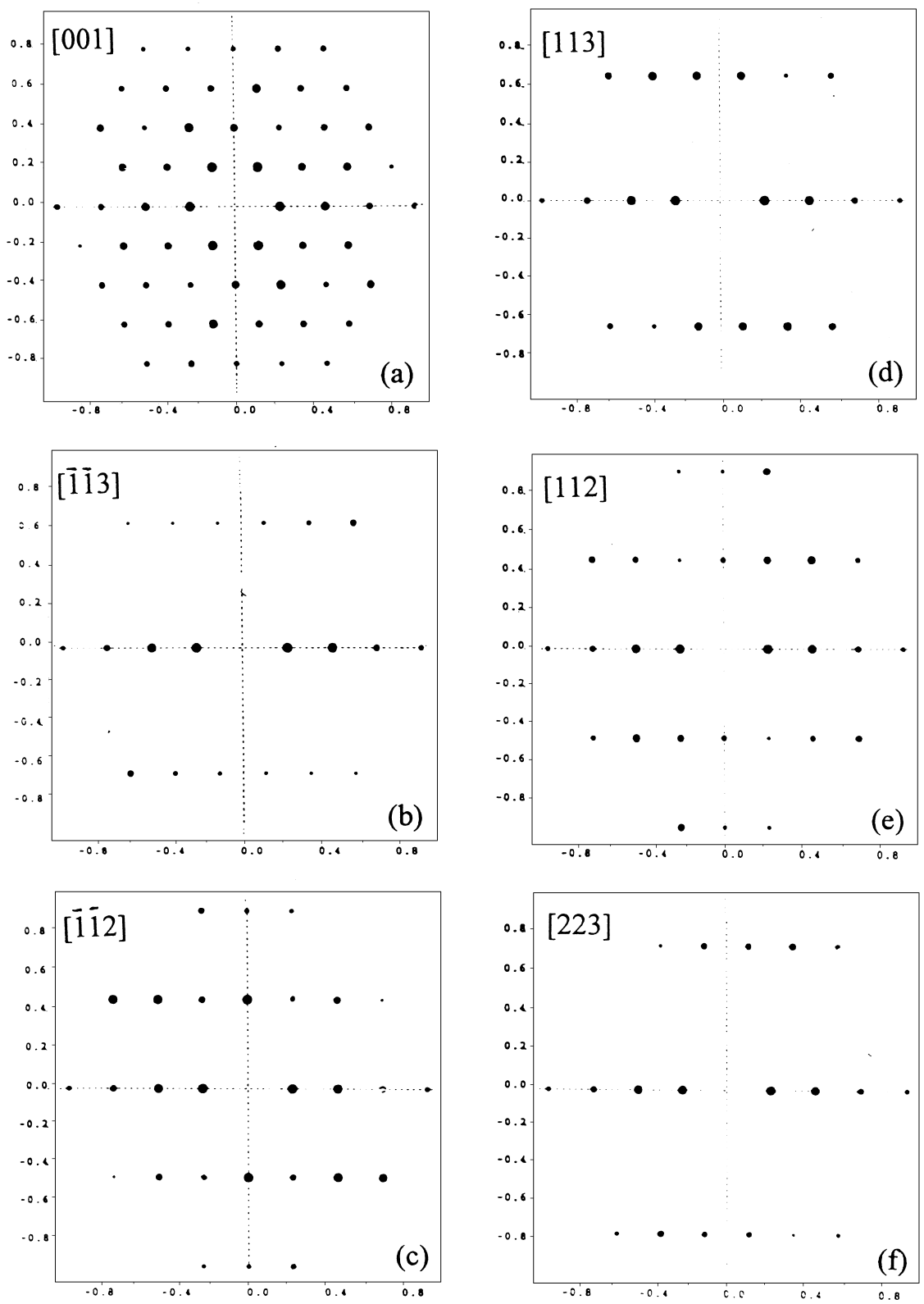

Figure 8 Simulated electron diffraction pattern for tilt ED patterns around *a**

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