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Polymer Structure Determination Using Electron Diffraction Techniques

The crystallographic structure of organic crystals is most commonly studied using x-ray diffraction (XRD) techniques. Unfortunately, rather large crystals, at least 10^6 μm^3, are required for XRD analysis, and it is often quite difficult and sometimes impossible to prepare such large crystals. On the other hand, electron diffraction techniques, although not nearly as precise as XRD, do afford the capability of studying much smaller crystals. The minimum size for electron diffraction is on the order of 10^{-3} μm^3 (0.1 μm^2 area by 0.01 μm thick). Since most polymer crystals are very sensitive to radiation damage caused by the beam in the electron microscope, special precautions must be taken to minimize beam damage to the specimen. Our approach to minimizing radiation damage, while still obtaining usable diffraction data, is described in terms of using the condenser-objective lens optics of the Philips 301 S(TEM) electron microscope. Three examples of the application of electron diffraction structure analysis are given. These include the structures of halogenated polysulfur nitride $(SN)_x$, neutral α,α′-polypyrrole, and poly(p-hydroxybenzoic acid) (PHBA).

Introduction

This paper is concerned with the study of the crystallographic structure of polymeric materials by means of transmission electron microscopy (TEM) and electron diffraction. It must be emphasized that x-ray diffraction is the preferred method for crystallographic structure analysis; it should be used whenever possible since the precision and accuracy of x-ray diffraction are much better than those of electron diffraction. The major limitation to the use of x-ray diffraction relates to the specimen size. For structure determination of single crystals using x-ray diffraction, the material being analyzed should have a volume of at least 10^6 μm^3 (i.e., ≈100 μm on a side). In many cases it is either extremely difficult or simply impossible to grow polymeric single crystals of this magnitude. However, electron diffraction patterns may be routinely obtained from polymer single crystals having volumes of only 10^{-3} μm^3 (0.1 μm × 0.1 μm × 0.01 μm thick), or about nine orders of magnitude smaller! Under special circumstances, to be discussed, electron diffraction has been obtained from isolated polymer single crystals that were 10 nm on a side, or 10^{-6} μm^3 in volume.

We briefly discuss some of the experimental problems and the methods we have developed to study beam-sensitive materials in the electron microscope. Results obtained from the application of these techniques to the determination of the crystallographic structure of polypyrrole and poly(p-hydroxybenzoic acid) (PHBA) are given. A detailed report concerning the application of electron diffraction techniques to study the structural behavior of halogenated polysulfur nitride, $(SN)_x$, has been published in Ref. [1].

Experimental details

Unfortunately, many polymers are very susceptible to radiation damage from the electron beam. One measurable result of this damage is loss of crystalline order in the material. In fact, for many polymers crystalline order is destroyed so quickly that it is difficult to obtain electron diffraction patterns at all. Part of this difficulty arises because polymers are composed of elements with low atomic numbers (C, O, N, etc.), and elastic scattering of high-energy (i.e., 100-keV) electrons by such elements is relatively weak. As a result, the intensities of the diffraction maxima are weak, and long exposure times are often required to photograph the diffraction patterns. It follows that the specimen may be destroyed before sufficient data can be collected. To combat such problems of radiation damage, "low-dose" techniques must be used. With these techniques, the rate of damage and/or the total dose of electrons is reduced, and improved schemes are used for collecting the transmitted electrons.

Many experimental techniques have been used to reduce the electron dose rate at the specimen and to improve the electron collection efficiency. The most routine of these include 1) undersaturating the tungsten filament in the electron gun, 2) using smaller apertures in the illumination (condenser) system, 3) photographing at the lowest image magnification possible commensurate with the required image detail, 4) using high-speed electron image photographic film, and 5) processing the film for maximum speed.

The rate of specimen damage may also be reduced either by cooling the specimen or by using higher accelerating voltages. Knapek and Dubochet [2], operating at 4 K and 220 keV, report reductions in damage rates of 30 to 370 times, compared to the same materials irradiated at 300 K and 80 keV. More typically, reduction factors of two to ten times are reported when reduced temperatures are used at 80–100 keV [3]. Reduction factors of two to three times have been reported for 1-MeV accelerating voltages [4]. The results reported here were mostly obtained for operation at 300 K and 100 keV.

In standard transmission electron microscope (TEM) operation, the incident beam is spread over a large area of the specimen in order to provide more coherent illumination for imaging. Diffraction patterns from small areas are obtained under this broad illumination by placing a field-limiting aperture in the image plane of the objective lens, which is conjugate to the specimen plane. This technique is called *selected area diffraction* (SAD). Spreading the beam over a large area reduces the dose rate to the specimen, but unfortunately this same large area of the specimen is illuminated, even though only a small portion of that area is observed on the viewing screen. In other words, a large area of the specimen is being exposed to the same damaging radiation dose as the area being viewed. Thus, when the dose is sufficient to destroy the area of the specimen under study, a large area not in view has been destroyed at the same time. It is imperative for optimal low-dose operation to limit the irradiated area of the specimen to that which is seen on the viewing screen.

In modern TEMs, especially those with scanning attachments that allow scanning transmission electron microscopy, S(TEM), the objective lens is operated at a much higher excitation than in a conventional TEM. What is achieved in many cases is that the final aperture of the illuminating system, the second condenser (C2) aperture, is imaged onto the specimen plane. That is, the plane containing the C2 aperture is made conjugate to the specimen plane. Consequently, the C2 aperture acts as a field-limiting aperture at the specimen [5]. This image of the C2 aperture is in focus at the specimen plane and is reduced in size by a demagnification factor M_d; M_d is approximately equal to L, the distance between the C2 aperture plane and the specimen plane, divided by f_o, the focal length of the objective lens. For a typical S(TEM), $L = 100-150$ mm and $f_o = 3.0$ mm; thus, $M_d = 30-50$. The consequence of this electron-optical configuration, referred to as the condenser-objective mode [6], is that the area of the specimen inside the image of the aperture is the only area of the specimen exposed to the electron beam. Hence, the problem of global irradiation of the specimen is eliminated in favor of very localized irradiation.

By combining condenser-objective lens optics with a coupled set of deflection coils located in front of and behind the specimen, it is possible to deflect the beam onto an area of the specimen near to, but off, the optical axis of the microscope, while still observing the area on the viewing screen for purposes of focusing and correcting for aberrations [7]. Disabling the deflection system just prior to exposing a photographic film shifts the incident beam to the optical axis of the microscope. Thus, the recorded image comes from an area of the specimen which had not been previously irradiated by the electron beam. In a slightly different approach, the incident beam is deflected off axis above the C2 aperture; this is known as *beam-blanking* [8]. After focusing, etc., a new area of the specimen is translated onto the optical axis of the microscope, and the beam deflection is disabled just prior to exposing the photographic film. Again, the recorded image is from a nonirradiated area of the specimen.

Since the illuminated area of the specimen is field-limited by the demagnified image of the C2 aperture, there is no need to use the standard approach to selected area diffraction described previously. In the condenser-objective mode, the size of the area selected is determined by the size of the C2 aperture and by the demagnification factor. The size may be varied by using a range of aperture sizes in the C2 aperture holder. With the Philips 301 S(TEM), the demagnification factor $M_d = 35$. Inserting apertures having diameters of 500, 100, or 10 μm in the C2 holder gives selected areas of approximately 14, 3, or 0.3 μm in diameter, respectively. We have used apertures with diameters as small as 1.0 μm in C2, giving a selected area diffraction (SAD) diameter of 30 nm. Such apertures are not used routinely, however, since the alignment of so small an aperture over a particular region of interest on the specimen is very tedious. In addition, the intensity of the diffraction pattern is so weak that exposure times in excess of one minute are required. Specimen drift then becomes a factor in determining the final dimension of the area which gives rise to the recorded diffraction pattern. For most of the work reported here, 5-, 10-, or 100-μm apertures were used in the C2 to define the SAD; exposure times were less than or equal to 16 seconds.

To determine the crystallographic structure of a crystal, it is necessary to obtain diffraction patterns from different orientations of the crystal. Using a 5-μm C2 aperture in the condenser-objective lens mode, it is possible to obtain diffraction patterns from a few different orientations from one single crystal a few hundred nanometers in diameter. To do this, the crystal is tilted between micrographs, and the image of the aperture is simply shifted to a new nonirradiated region of the crystal just prior to exposing the photographic film. However, if the single crystals are very small (i.e., less than 100 nm in diameter) it may be necessary to use different crystals for each diffraction pattern, if the dose accumulated in a single exposure is sufficient to destroy the entire crystal.

Results

The analysis of the crystallographic structures of polypyrrole and poly(p-hydroxybenzoic acid) (PHBA) is presented. Although for quite different reasons, in both cases the required experimental data could only be obtained by using electron diffraction techniques. In the case of poorly crystalline polypyrrole, the x-ray diffraction gave completely structureless patterns containing no maxima. Electron diffraction, although not giving sharply defined maxima, did yield easily discernible diffuse peaks to which *d* values, or interplanar spacings, could be assigned. The problem encountered using x-ray diffraction to analyze PHBA was almost the opposite. The PHBA is highly crystalline, and x-ray diffraction patterns contained well-defined diffraction maxima. Unfortunately, due to the small size of the individual crystallites of PHBA, typically less than 1 μm on edge, the only x-ray diffraction patterns obtainable were powder patterns from an array of crystals. As is usually the case with powder patterns from organic crystals, an insufficient number of diffraction maxima were obtained to allow analysis of the crystallographic structure. However, by using electron diffraction, it was possible to obtain single-crystal patterns from individual crystallites and thus to construct a structural model.

Both polymers are moderately beam-sensitive, and extensive precautions had to be taken to minimize radiation damage during the course of the investigation in the TEM. These included undersaturating the filament, setting the C1 lens current to maximum, using small C2 apertures, and processing the film for maximum speed.

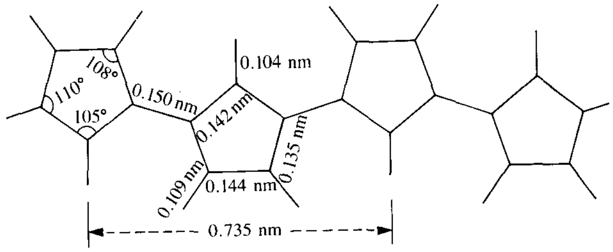


Figure 1 Linear chain structure for neutral α,α'-polypyrrole.

- *Polypyrrole*

Polypyrrole is a polymer formed by the linking of individual pyrrole rings, bonded predominantly via the α,α' carbons with alternating nitrogen atoms, as drawn in Fig. 1. (See the companion papers by Clarke et al. [9] and Diaz et al. [10] in this issue.) This configuration gives rise to a linear chain structure, as opposed to a ringlike structure which would result from nonalternating nitrogen atoms all pointing toward the center. Thin films of polypyrrole are prepared by the electrochemical oxidation of pyrrole using dried deoxygenated acetonitrile and silver perchlorate in a dry box [11]. Chemical analysis shows that there are approximately three pyrrole rings per perchlorate anion. Films of neutral polypyrrole are obtained by electrochemically reducing the oxidized films.

Polypyrrole has been very difficult to characterize because no solvent has been found and no structural information could be obtained from x-ray diffraction studies. Although polypyrrole is predominantly α,α'-bonded, the presence of other bonding, which has been shown from IR and NMR studies, has undoubtedly led to structural disorder in the polymer. Such structural disorder has made the interpretation of much of the characterization data [11] difficult. In order to eliminate these alternate bonding schemes, polypyrroles have been synthesized with both β positions of the pyrrole ring blocked by methyl groups. This ensures exclusive α,α' bonding along the polymer chain. In the case of poly(β,β'-dimethylpyrrole) (PBDMP), blocking of the β carbons has led to increased order along the polymer chain and a measurable improvement in the crystallinity of the polymer. Electron diffraction data obtained from films of PBDMP were crucial in developing the structural model of neutral polypyrrole presented here.

Electron microscope specimens were prepared by ultramicrotomy of 0.5- to 2.0-μm-thick films of neutral α,α'-polypyrrole and from neutral PBDMP embedded in epoxy resin. Sections were made both parallel (planar section) and perpendicular (cross section) to the plane of the films. All sections were coated with approximately 10 nm of carbon prior to insertion in the TEM. It should be noted that

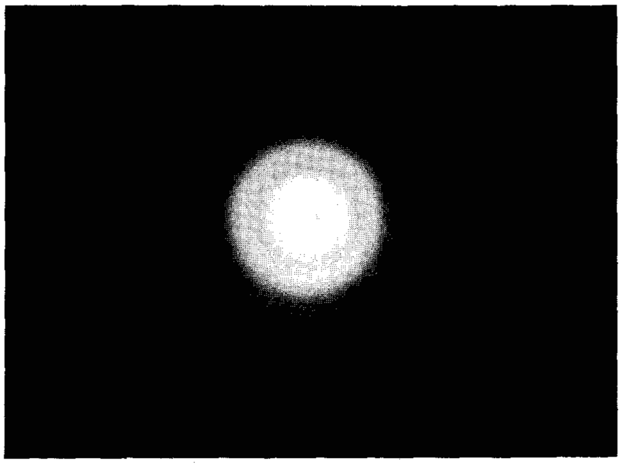


Figure 2 Electron diffraction pattern from a planar section of neutral α,α'-polypyrrole.

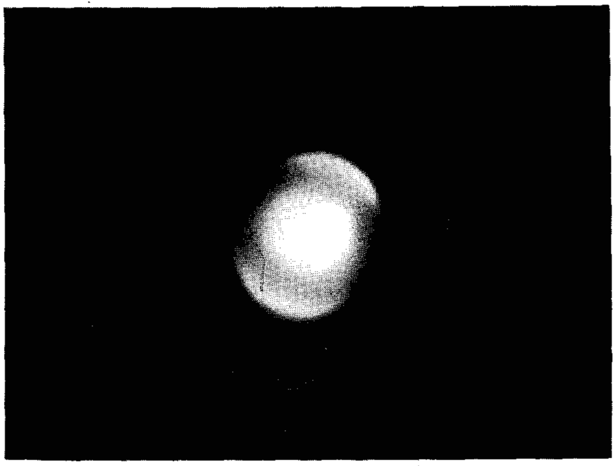


Figure 3 Electron diffraction pattern from a cross section of neutral α,α'-polypyrrole.

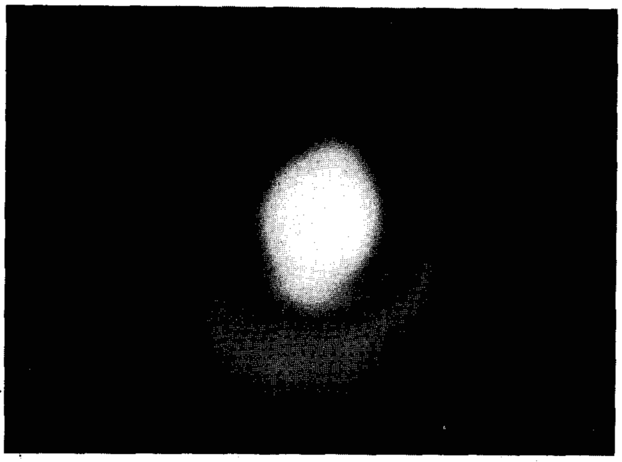


Figure 4 Electron diffraction pattern from a planar section of PBDMP.

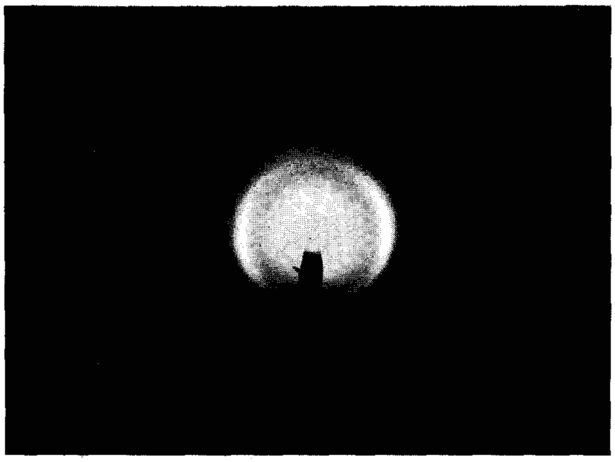


Figure 5 Electron diffraction pattern from a cross section of PBDMP.

samples of neutral polypyrrole react with air in the process of specimen preparation and contain approximately one oxygen atom per pyrrole ring; thus, they are no longer strictly neutral polypyrrole. Nevertheless, in this paper we refer to them as neutral polypyrroles to distinguish them from their electrochemically oxidized counterparts.

Typical electron diffraction patterns from the planar and cross sections are given in Figs. 2 and 3 for neutral polypyrrole and in Figs. 4 and 5 for PBDMP. The diffuse nature of the diffraction maxima is seen in all the patterns, indicating that both materials are poorly crystalline, although patterns from PBDMP are less diffuse, as predicted. These diffuse patterns are thought to originate in a structure consisting of small crystalline regions separated by much larger amorphous regions. The patterns from the planar section of PBDMP, Fig. 4, display a texture which suggests a preferred orientation of the polymer chains which is parallel to the plane of the film. Figure 2, from the planar section of neutral polypyrrole, shows no indication of texture and contains even fewer maxima; this indicates less ordering of the crystalline structure. It is believed in both cases that the polypyrrole chains lie with the pyrrole rings coplanar to the film surface. It is also believed that the crystalline regions are randomly

Table 1 Measured d values (in nm) from a collection of diffraction patterns for neutral polypyrrole and poly(β-dimethylpyrrole). For comparison, the tabulated interplanar spacings of graphite are included with the appropriate Miller indices, (hkl).

Neutral polypyrrole		*Graphite*		*Poly(β-dimethylpyrrole)*	
Planar section	*Cross section*	*d value*	*(hkl)*	*Planar section*	*Cross section*
0.365	0.341	0.336	002	0.51–0.33*	0.365
0.217	0.216	0.203	101	0.308	0.310
0.178	0.178	0.168	004	0.226	0.226
0.135	0.135	0.123	110	0.173	—
0.114	0.114	0.112	006	0.134	0.136
				0.113	0.117

*Elliptical.

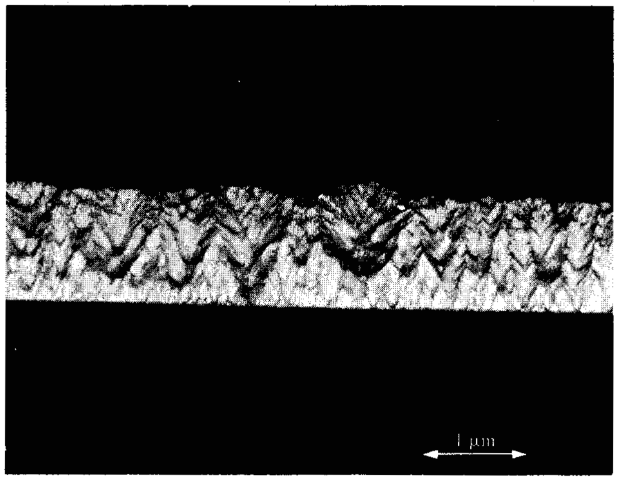


Figure 6 Dark-field electron micrograph from a cross section of neutral α,α'-polypyrrole. The image was taken with the objective aperture sampling a portion of the first maxima in the diffraction pattern seen in Fig. 3.

oriented in the neutral polypyrrole, and have some preferred orientation in PBDMP. Diffraction patterns from cross sections of neutral polypyrrole and PBDMP show a fiber texture (Figs. 3 and 5), again suggesting that the polymer chains are aligned parallel to the surface of the prepared film. A characteristic d value of 0.341 nm is obtained from diffraction patterns from the cross sections of neutral polypyrrole films. This value is very close to the basal spacing observed for graphite, $d_{002} = 0.336$ nm, indicating that the separation between chains is determined by the π,π molecular-orbital interaction of the pyrrole rings. Dark-field electron micrographs taken from a cross section of neutral polypyrrole using the 0.341-nm diffraction maxima are not unlike similar images obtained from pyrolytic graphite (see Fig. 6). This further supports the structural arguments just presented. In PBDMP, this characteristic spacing increases to 0.365 nm, as might be expected since the interplanar spacing is affected by the methyl groups.

By careful measurement of a number of diffraction patterns from both planar and cross sections of the various polypyrroles, it is possible to arrive at a collection of d values which is a faithful representation of the structure. The results of these measurements are given in Table 1 for both neutral polypyrrole and neutral poly(β-dimethylpyrrole), along with tabulated data for graphite.

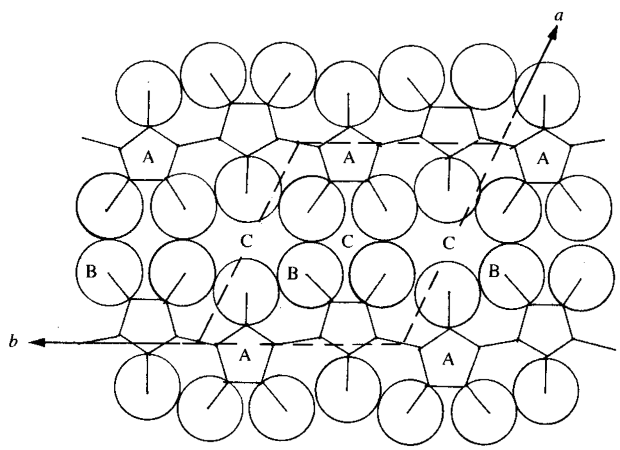


Figure 7 Proposed arrangement of the chains in the first layer of neutral polypyrrole. The circles represent the van der Waals diameters of the hydrogen atoms. The locations marked B represent the positions of pyrrole rings, A, in the second layer of the ABAB stacking. Positions marked C are probable locations for anion intercalation. The a and b axes of the proposed monoclinic unit cell are indicated. The c axis is normal to the plane of the figure.

Assuming that the polypyrrole chain is indeed linear and planar with alternating nitrogens, and that the dimensions of the pyrrole ring of the monomer apply, it is possible to quantitatively describe the chain geometry. The value of the pyrrole-pyrrole bond is assumed to be the same as that of the ring-ring bond in polyphenylene. These assumptions give rise to the geometry shown previously in Fig. 1, with the unit translation along the chain equal to 0.735 nm.

On the basis of this chain geometry, the measured graphitelike structure, and other interplanar spacings, it was possible to construct a model structure for neutral polypyrrole. The proposed structure has a monoclinic unit cell with $P2_1/a$ symmetry. That is, the unit cell contains a screw axis parallel to the c axis and a glide plane along the a axis. The proposed structure consists of planes of chains arranged as shown in Fig. 7, stacked in an ABABAB. . . sequence, with

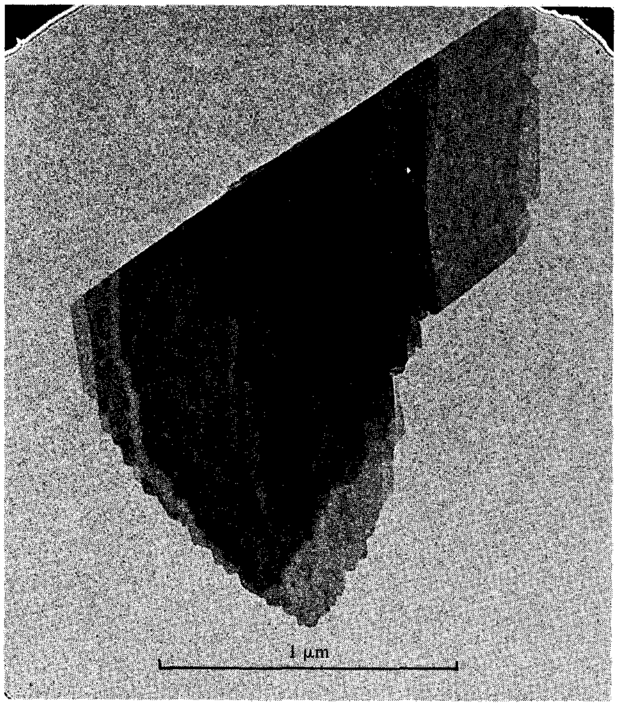


Figure 8 Electron micrograph of a small lamella of a tetramer of PHBA. The thinnest regions are probably 5 nm thick. Five-nm increases in thickness may be defined by increments in contrast in the image.

Table 2 Interplanar spacings for the planar and cross sections of polypyrrole. Measured values were obtained from electron diffraction patterns from neutral α,α'-polypyrrole and calculated values are based on the model presented here. All d values are in nm.

Planar section			*Cross section*		
Measured	*Calculated*	*(hkl)*	*Measured*	*Calculated*	*(hkl)*
0.365	0.365	200	0.341	0.341	002
0.217	0.218	030	0.216	0.218	030
0.178	0.183	400	—	0.213	100
0.135	0.135	420	0.172	0.169	004
0.114	0.114	340	0.135	0.135	420
			0.114	0.112	006

the alternate planes aligned so that the "A" pyrrole ring is over the "B" location. Lattice constants for the monoclinic unit cell are $a = 0.82$ nm, $b = 0.735$ nm, $c = 0.682$ nm, $\alpha = \beta = 90°$, and $\gamma = 117°$. The volume of the unit cell is 0.366 nm^3 and, based on the chain conformation, contains four monomer units per unit cell. As mentioned earlier, the neutral α,α'-polypyrrole studied was probably in an oxidized state with approximately one oxygen atom per pyrrole ring [12]. Using these data, the density of the polymer is calculated to be 1.47 g/ml. The oxygen species do not seem to intercalate between the basal planes as might be expected, but rather appear to intercalate between the chains within the plane, probably at either of the two positions indicated by "C" in Fig. 7. The diffraction measurements support this argument since the 00l interplanar spacings between basal planes are only slightly affected by the presence of various dopants. Data obtained from a cross section of α,α'-polypyrrole perchlorate are almost identical to those given in Table 1 for neutral α,α'-polypyrrole. The slight increase in the d values from the cross section of the PBDMP may be completely accounted for as due to the methyl groups attached in the β bond positions of the pyrrole. In Table 2, d values calculated from this model are compared with the measured d values from neutral polypyrrole. The fit is excellent, considering the diffuse nature of the experimental diffraction patterns.

Polypyrrole is a very beam-sensitive material, on the basis of observations made during this study. In order to be able to photograph the diffraction patterns, it was necessary to expose the photographic film to a fresh region of the specimens as quickly as possible. This was done while operating the microscope at a dose rate of 2×10^{-4} A/cm^2, a condition which could only be achieved by operating the filament in the electron gun in an unsaturated mode. Under this dose rate, a diffraction pattern would disappear from view in 10 to 15 seconds. This means that the critical dose for neutral polypyrrole is approximately 2×10^{-3} C/cm^2 for the complete loss of the diffraction pattern at 100 keV. For comparison, the critical doses for complete loss of the diffraction pattern from polyethylene and phthalocyanine are approximately 10^{-2} and 10^{-1} C/cm^2, respectively (see Table 2).

- *Poly(p-hydroxybenzoic acid)*

The crystalline structure of poly(p-hydroxybenzoic acid), PHBA, has been the subject of a number of studies recently [13–15]. This activity follows earlier work in which a double helix structure with two chains in a reversed head-to-tail order was proposed [16]. This double helix structure was based on data obtained using x-ray powder diffraction and selected-area electron diffraction. The assignment of the threefold symmetry in Ref. [16] was based on the interpretation of an electron diffraction pattern from an array of small crystallites. This interpretation has been questioned in the last several years. Hay [13] in 1981 noted the strong similarity in x-ray powder diffraction patterns between oriented copolymers of PHBA and the PHBA homopolymer. He proposed an orthorhombic unit cell rather than the double helix structure with threefold symmetry. Recently, Lieser [14] also proposed a similar orthorhombic structure based on electron diffraction results he obtained.

Our effort to reconfirm the existence of the double helix structure started several years ago. The goal was to use the

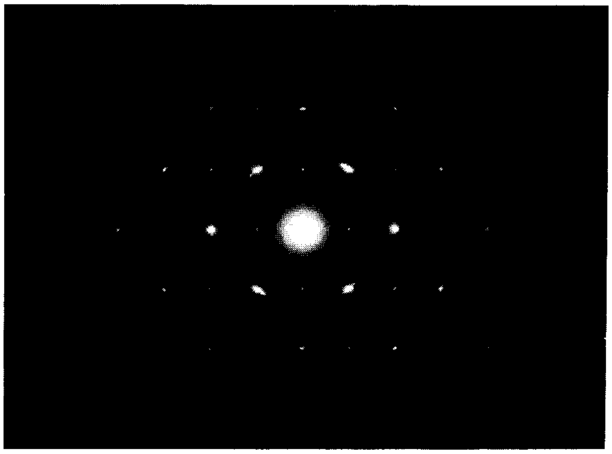


Figure 9 Electron diffraction pattern from the basal plane of PHBA. The molecular weight of this specimen was greater than 50 000, but similar diffraction patterns were obtained from tetramer and higher in molecular weight.

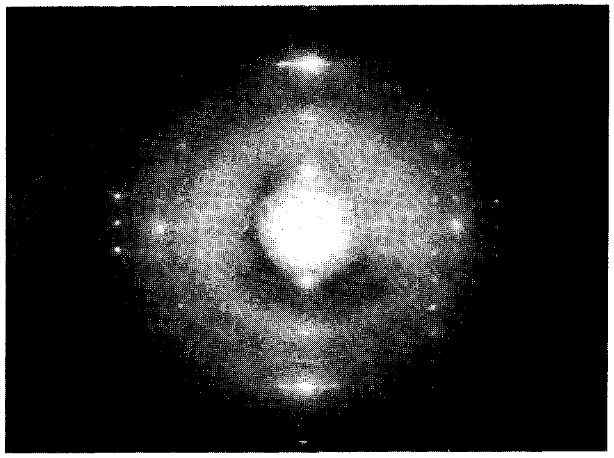


Figure 10 Electron diffraction pattern from a fibrillar specimen of PHBA showing that the c axis (north-south in the image) is normal to the basal plane (east-west in the image).

special electron diffraction capability of the condenser-objective lens in the Philips 301 S(TEM) to obtain single-crystal diffraction patterns at different orientations from various PHBA polymer crystals. These data would then be used to determine the crystal structure of the PHBA.

The homopolymer of PHBA was prepared by polymerization of p-acetoxybenzoic acid. Details of the preparation have been described earlier [17]. Molecular weights of the polymers ranged from tetramer to greater than 20 000. The polymers were in powder form with the individual particles in the powder having a lamellar structure. Samples for TEM were prepared by impact-fracturing the powder at liquid nitrogen temperatures and ultrasonically dispersing the resulting lamellae in alcohol. A drop of the alcohol-PHBA suspension was allowed to dry on carbon-coated 200-mesh copper electron microscope grids. The resulting specimen consisted of a dispersion of PHBA lamellae or microfibrils, depending on the pretreatment of the material, some of which were thin enough to provide sharp single-crystal electron diffraction patterns. Most lamellae are less than one micron in diameter and a few tens of nanometers thick. An example of a typical lamella obtained from PHBA tetramer is shown in Fig. 8. On the basis of our structure analyses, to be discussed, it is estimated that the thinnest region of this specimen is approximately 5 nm thick, and that thickness increases in 5-nm increments can be seen in the image.

Single-crystal electron diffraction patterns were usually obtained easily from similar specimens. A typical example obtained from a lamella of high-molecular-weight PHBA is shown in Fig. 9. Due to the lack of a fiber texture in such patterns, it was assumed that they are representative of the basal plane orientation. On the other hand, when microfibrils were found, that is, specimens containing the fiber axis of the polymer, diffraction patterns as shown in Fig. 10 were obtained. Inspection of these two patterns shows that they possess quite different characteristics. The diffraction pattern from the lamellae, or basal plane, clearly shows twofold tetragonal symmetry. Miller indices may be assigned to the diffraction spots, which is a representation of the reciprocal lattice of the crystal, and the basal plane lattice vectors, a and b, determined. In Fig. 10, the fiber axis clearly defines the c axis of the unit cell which is perpendicular to the $hk0$ plane. Again, assigning Miller indices to the diffraction maxima provides a measure of the unit cell repeat vector, c, along the fiber axis. The point group of the structure has been determined to be orthorhombic since the lattice vectors $a \neq b \neq c$, and the interaxial angles $\alpha = \beta = \gamma = 90°$.

Analysis of the diffraction data gives the following values to the unit cell vectors: $a = 0.762$ nm, $b = 0.570$ nm, and $c = 1.256$ nm. The unit cell volume is thus 0.546 nm^3, and using the monomer chemical formula of $C_7H_4O_2$ yields a calculated density of 1.46 g/cm^3, with four chemical formula units per unit cell. Analysis of the extinctions in the diffraction patterns (e.g., $h00$: $h = 2n$, $0k0$: $k = 2n$ and $00l$: $l = 2n$) suggests that the space group of the orthorhombic unit cell is $P2_12_12_1$, which provides for three orthogonal but nonintersecting 2_1 screw axes.

Due to the high melting point of poly(p-oxybenzoate) and the tendency of p-hydroxybenzoic acid to decarboxylate at elevated temperatures, the so-called homopolymer of PHBA is actually obtained by a heterogeneous solution polymerization of p-acetoxybenzoic acid in a heat-transfer medium

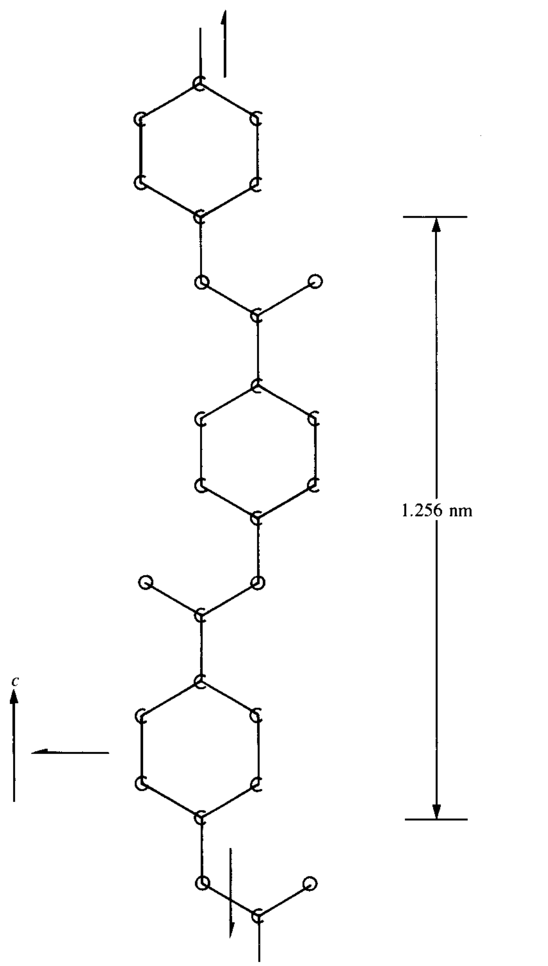


Figure 11 Proposed chain structure of PHBA, which lies parallel to the c axis; cis conformation of the chain may be seen. The two orthogonal screw axes are indicated.

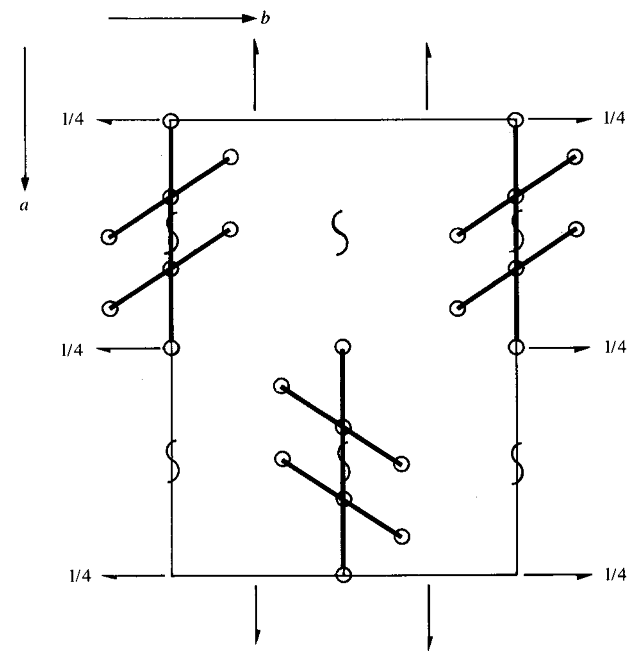
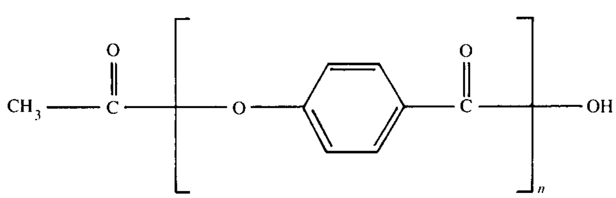


Figure 12 Proposed structure of the basal plane showing the arrangement of the PHBA chains and the location of the three nonintersecting screw axis symmetry elements.

[16]. The resulting polymer backbone is identical to the hypothetical homopolymer p-hydroxybenzoic acid, except for acetoxy end groups, and consists of parasubstituted phenylene rings linked by ester groups and terminated by acetoxy and carboxylic acid groups, as illustrated below. The repeat distance of the phenyl-ester group is 0.628 nm.



The measured c axis is twice this repeat distance and also contains a 2_1 screw axis. Thus, the suggested polymer chain configuration consists of an all-cis structure, with the ester group at an angle of 57° to the phenyl ring. A two-dimensional representation of this is given in Fig. 11. Since there are two monomer units per unit cell along the polymer chain, and there are four monomer units per unit cell, there must be two polymer chains in each unit cell. Considering the other required symmetry elements, a model for the basal plane structure may be derived and is shown schematically in Fig. 12. All the symmetry requirements are thus met with a model that fits into the physical space of the unit cell.

The PHBA crystallites were beam-sensitive, but not nearly as much as the polypyrrole. Complete diffraction pattern disappearance occurred typically after a dose of 10^{-2} C/cm^2, which is five times greater than for polypyrrole. This permitted, working quickly, the photographing of two or sometimes three diffraction patterns of different orientations of the same crystallite.

Conclusion

A brief discussion of the use and advantages as well as the disadvantages of transmission electron microscopy in studying beam-sensitive materials has been given. Examples of the crystal structure analysis of two polymers, polypyrrole and poly(p-hydroxybenzoic acid), were given in some detail. The final test of a structure analysis is the comparison of calculated diffraction intensities for the model proposed with the experimentally measured values. This work is currently under way for the two structures presented here.

The electron microscope can be used quite successfully to determine the crystal structure of beam-sensitive materials by modern techniques which reduce the beam damage to the specimen. The strength of electron microscopy lies in the relaxed requirements for specimen size when compared with x-ray diffraction. Its weakness lies in the limited precision of the diffraction data experimentally obtained.

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