Electron diffraction studies of the structure of polyaniline–dodecylbenzenesulfonate

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Polyaniline–dodecylbenzenesulfonate (PANI–DBSA) fibrils prepared directly during emulsion polymerization or by precipitation from solution have been studied by transmission electron microscopy. High-aspect-ratio fibrils are obtained with typical dimensions of order 1 mm by 1 μm. The small crystallites within the fibrils are oriented with c axis parallel to the fibril axis. The crystal structure of the PANI–DBSA crystallites has been determined as orthorhombic with two PANI chain repeat units and two DBSA molecules in the unit cell; the lattice parameters are $a = 1.178$ nm, $b = 1.791$ nm and $c = 0.716$ nm. Based on this structure, the calculated density is 1.12 g cm^{-3}. The systematic absences in the PANI–DBSA diffraction data are consistent with those expected for the *Pmnm* space group.

(Keywords: polyaniline fibrils; dodecylbenzenesulfonate; electron diffraction)

INTRODUCTION

The use of functionalized sulfonic acids (with surfactant counter-ions) for protonating polyaniline (PANI) has enabled processing of this important conducting polymer from solution, in the conducting form, using common organic solvents[1–3]. The ability to cast the material from solution under controlled conditions provides an opportunity for analysis of the crystal structure of the emeraldine salt form with surfactants such as dodecylbenzenesulfonate (DBSA) as counter-ions. We have successfully prepared PANI–DBSA fibrils directly during emulsion polymerization[4] and by precipitation from solution; the morphology and the crystal structure of these crystalline fibrils have been studied by transmission electron microscopy.

The crystal structures of the various forms of PANI with different counter-ions continue to be under active investigation. Subsequent to the discovery of relatively highly crystalline polyaniline[5] through precipitation from solution in sulfuric acid[6], there has been considerable effort directed towards control of the degree of crystallinity[7]. Attempts to establish the crystal structure and molecular packing have utilized X-ray diffraction from analogous salts of oligomers[8]. In addition, the local geometry within the PANI macromolecule has been calculated on segments of the polymer; for example, the torsion angles between adjacent carbon rings and between rings adjacent to a protonated nitrogen were investigated[9].

X-ray diffraction data from the various forms of PANI have been reported[5,7,10]. However, these data (typically limited in the number of observable diffraction peaks) are principally powder patterns, obtained from diffraction by randomly oriented small crystallites within the samples. Limited X-ray diffraction data have been obtained from stretched films with modest draw ratios ($\lambda = 3$)[7].

In contrast, transmission electron microscopy (TEM) can determine the local morphology and the corresponding diffraction pattern, simultaneously, from the area with dimensions as small as 1 μm. The orientation of the small crystallites can be determined from comparison of the features on the diffraction pattern with the local morphology (e.g. orientation of the polymer fibrils). Thus, when it is possible to prepare samples that are suitable for TEM, electron diffraction crystallography has some clear advantages.

We have utilized the novel processing features of PANI–DBSA to fabricate oriented fibrils suitable for TEM analysis, and here we report the results of a diffraction study of the structure of these samples. The crystal structure of PANI–DBSA was determined to be orthorhombic with two PANI chains per unit cell and one DBSA molecule associated with each of the chains in the unit cell. The repeat unit can, therefore, be described as $(\text{-}\phi\text{-NH-}\phi\text{-NH-})^{+}(\text{DBSA})^{-}$, as shown schematically in *Figure 1*; here ϕ denotes a phenyl ring. The lattice parameters are $a = 1.178$ nm, $b = 1.791$ nm and $c = 0.716$ nm. Based on this structure, the calculated density of crystallites is 1.12 g cm^{-3}. The systematic absences in the PANI–DBSA diffraction data are consistent with those expected for the *Pmnm* space group.

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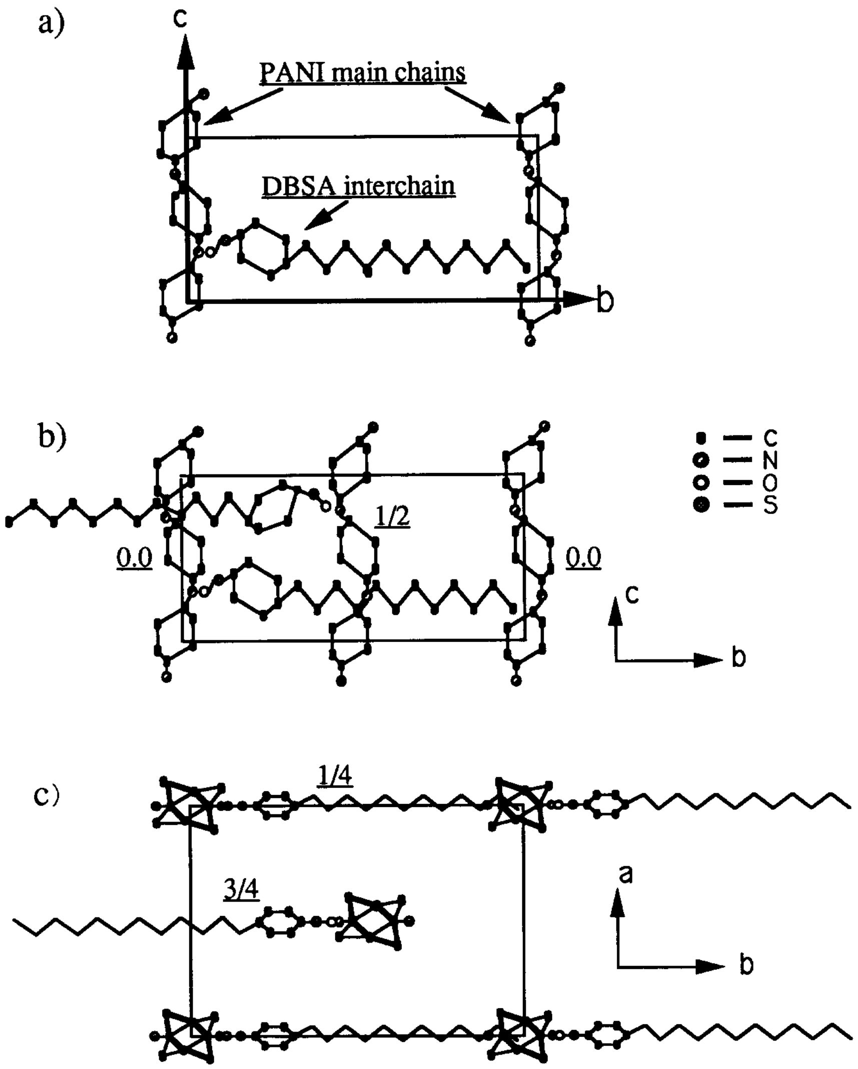


Figure 1 (a) Schematic drawing of the main chains and the interchain packing. (b) Projection of the PANI–DBSA unit cell on the *bc* plane. (c) Projection of the PANI–DBSA unit cell on the *ab* plane. Note that the hydrogen atoms were omitted

EXPERIMENTAL

Fibril formation

The PANI–DBSA fibrils designated at F1 and F2, respectively, were prepared by two independent methods. The F1 fibrils are obtained directly from emulsion polymerization, as follows. A solution of 0.95 g (0.015 mol) aniline (Aldrich), 5.00 g (0.01 mol) DBSA and 10 g xylene was prepared. To this solution was added 30 g of distilled water to form a viscous emulsion. Polymerization was initiated by the addition of 1.82 g (0.008 mol) of $(NH_4)_2S_2O_8$ in 10 g of distilled water, so that the molar ratio of DBSA to aniline was 1.5 and the molar ratio of oxidant to aniline was 0.8. The polymerization was carried out for 6 h at 25°C. The PANI–DBSA F2 fibrils are obtained by precipitation of the PANI–DBSA complex from toluene containing poly(methyl methacylate) (PMMA). A 1% (w/w) PANI–DBSA solution was added to 5% (w/w) of PMMA in toluene while stirring. The PANI–DBSA complex precipitated as long, oriented fibrils.

Sample preparation for TEM

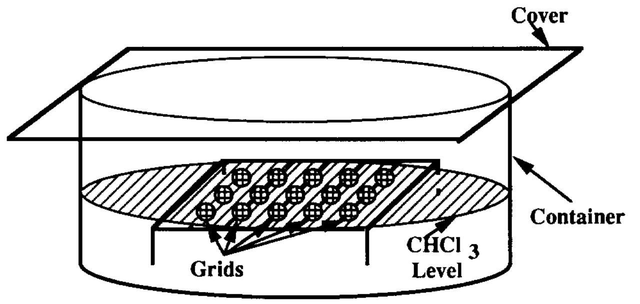


Figure 2 Schematic drawing of the extraction of the PMMA from the polyblend film, leaving F2 fibreils on the TEM grids

The F1 fibrils were picked up on TEM grids from a suspension of the fibrils in acetone, and subsequently coated with a thin carbon film (about 10 nm) and dried. The F2 fibrils were prepared for TEM examination by casting the blend dispersion of PANI–DBSA fibrils with PMMA onto glass slides, making a film of about 100 nm in thickness, and dried. The film was then coated with a layer of carbon (thickness about 10 mm). The carbon-coated film was peeled off the glass and cut into small pieces, each with diameter around 3 mm. The latter were then put on TEM grids with the carbon film up. The grids carrying the film were gently placed on a 'holey plate' (*Figure 2*), which was immersed in chloroform with the liquid level just over the surface of the plate and at the bottom of the grid in order to dissolve the PMMA. The fibrils were converted to the emeraldine base form by compensation with 10% NH_4OH aqueous solution for 5 h.

In order to define the main-chain direction, drawn films of PANI–DBSA in polyethylene were investigated by TEM. First, 20 g of PANI–DBSA solution (0.3% w/w) in xylene was mixed with 0.15 g of ultra-high-molecular-weight polyethylene (UHMW PE, Hostalen GR 412, average molecular weight 2×10^6) and 0.01 g of antioxidant, and heated in an oil bath at 126.6°C for 1 h. The resulting hot solution was cast onto an aluminium plate. Xylene was removed by evaporation in air at room temperature. The PANI–DBSA complex content was 28.6%. The resulting PANI–DBSA/PE blend film was stretched on a hot plate at 105–115°C to a draw ratio $\lambda = 40$ (where λ is the ratio of the final length to the initial length). The TEM samples were prepared by thinning the drawn free-standing film with cellulose tape until the thickness was reduced to approximately 100 nm. This thin film was then carbon-coated, and the carbon-coated film was picked up on a TEM grid after flotation on water.

A JEOL EM100cx electron microscope, operated at 80 keV, was used for examination of the PANI–DBSA fibrils. The illumination was kept as low as possible to avoid radiation damage. The calibration for the diffraction data was carried out by coating an aluminium thin film (about 10 nm thick) onto the prepared TEM samples.

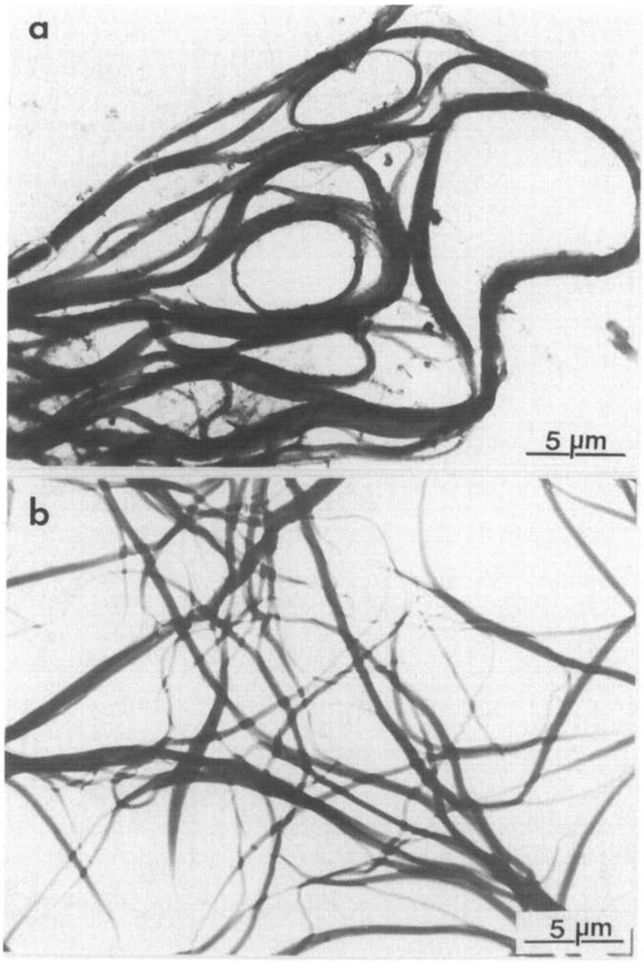


Figure 3 Electron micrographs of (a) F1 and (b) F2 fibrils

RESULTS AND DISCUSSION

The two methods described above produced entangled F1 and F2 fibrils, respectively (see *Figure 3*). *Figure 3a* shows the F1 fibrils, and *Figure 3b* shows the F2 fibrils. In both cases, the fibrils are of order 1 mm in length. The F1 fibrils have widths typically about 1 μm, while the F2 fibrils are somewhat thinner, with widths less than 1 μm. Selected-area diffraction patterns obtained from regions (with dimensions of approximately 1 μm) of F1 and F2 show the same features, indicating that the PANI–DBSA fibrils formed by the two different methods have the same crystal structure. The F1 fibrils have somewhat higher crystallinity than the F2 fibrils.

Figures 4a and *4b* are diffraction patterns from different segments of the F1 and F2 fibrils respectively. They show reflections with arcs of different length, indicating that the *c* axes of the crystallites are more nearly parallel to the fibril axis in the narrower part of the F1 fibrils (*Figure 4a*) than in the F2 fibrils (*Figure 4b*). The F2 fibrils and the wider portions of the F1 fibrils have longer length of arcs, as shown in *Figure 4b*.

In all the diffraction patterns obtained from PANI–DBSA, the reflections show broadened arcs in the *c*-axis direction (no sharp diffraction spots). This implies that the crystallites within the PANI–DBSA fibrils have an orientational order parameter:

$$f = \langle 3\cos^2\theta - 1\rangle/2 \leqslant 1$$

and a finite structural coherence length (ξ), which can be estimated from the Debye–Scherrer formula[11]:

$$\xi = 2\pi/\delta q$$

where θ is the scattering angle with respect to the symmetry axis and δq is the width of the Bragg reflection (along the symmetry axis). From analysis of the arc lengths from various segments of fibrils, we obtain a range of f values; for the best patterns, we find $f \approx 0.98$ for the c^*-axis reflections. From analysis of the width of the $\pm(0\,0\,2)$ reflections, we obtain $\xi \leqslant 30$ nm. Under dark-field imaging conditions, very fine crystallites can be seen (although the contrast in dark-field images is poor); the size of the crystallites can be estimated to be about 20–30 nm, consistent with the value of the coherence length inferred from the diffraction pattern. Comparison of the TEM image and the diffraction pattern from the imaged region indicates that the c^* axis (the vertical direction in *Figures 4a* and *4b*) corresponds to the principal axis of the fibril.

Diffraction from tensile drawn polyblend films of the PANI–DBSA in ultra-high-molecular-weight polyethylene (draw ratio $\lambda \approx 40$) gives an arc with the same *d* spacing as that of PANI–DBSA (i.e. the same as in *Figures 4a* and *4b*) with the c^* axis parallel to the draw direction (*Figure 4c*). Polarized optical and infra-red absorption measurements of such highly oriented films[12] unambiguously indicate that the PANI chains in the PANI–DBSA structure are parallel to the *c* axis.

We conclude, therefore, that the *c* axis is the polymer chain axis within the orthorhombic structure. Thus the fibrils grow with the PANI–DBSA chains parallel to the fibril axis with an orientational order parameter $f \approx 0.96$.

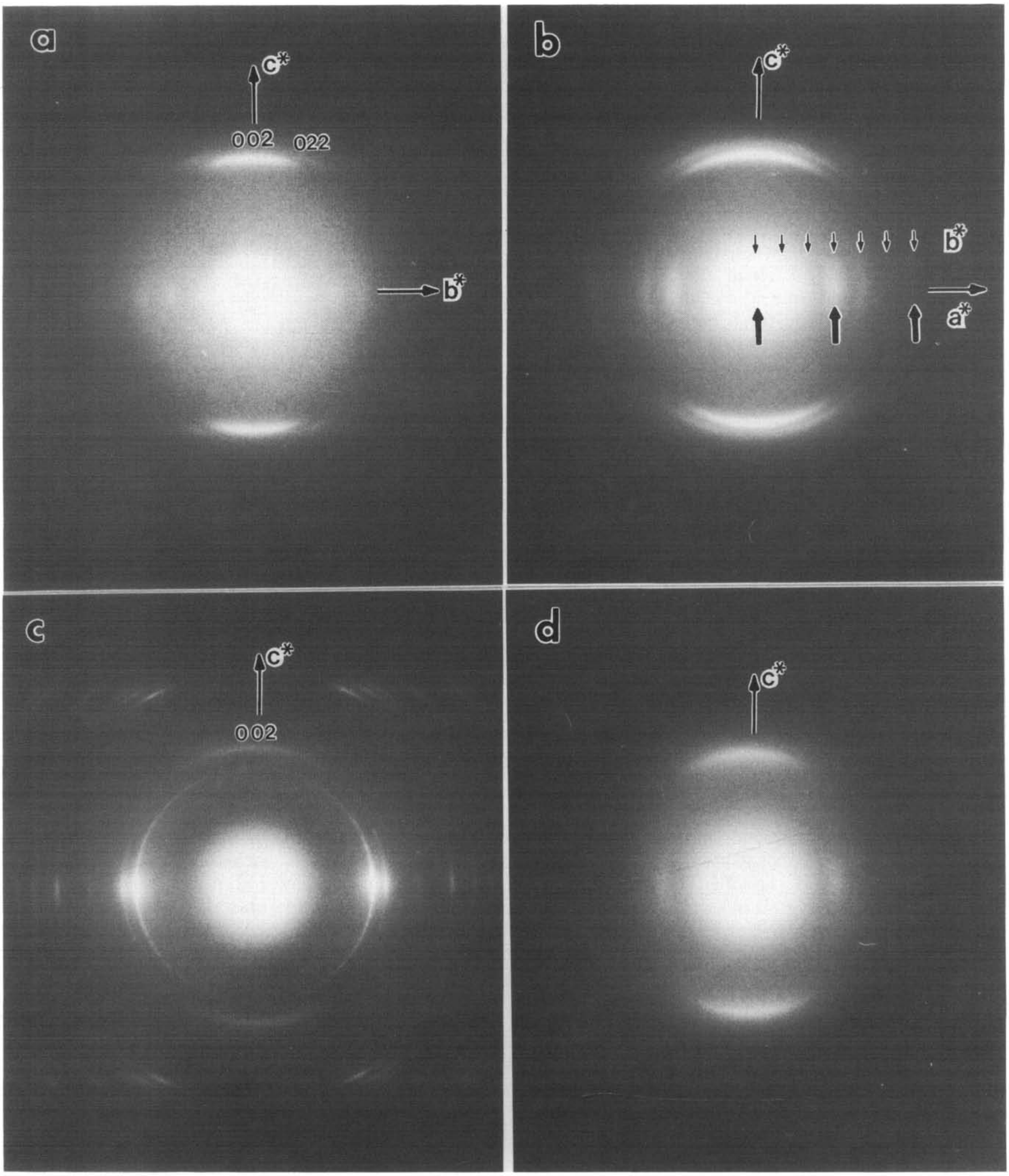
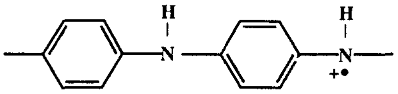


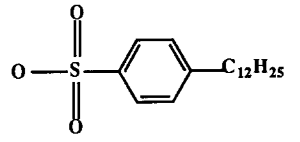
Figure 4 Electron diffraction patterns of the fibrils. (a), (b) Diffraction patterns from two different segments, showing different arc lengths for the (0 0 2) reflection; the corresponding order parameters are (a) $f=0.98$ and (b) $f=0.84$ respectively. The vertical arrows in (b) correspond to the inequivalent reflections shown schematically in *Figure 5* and listed in the first column of *Table 2*. (c) Diffraction pattern of the stretched PANI–DBSA blend with PE (draw ratio $\lambda=40$); the same $\pm(0\,0\,2)$ reflection can be seen. (d) Diffraction pattern from the fibril after reducing to the emeraldine base

The *c*-axis lattice parameter can be deduced from the diffraction patterns. Using the internal calibration provided by the aluminium diffraction rings, we find $c=0.716$ nm. Since one repeat unit of PANI, if straight, would have a length of approximately 0.542 nm (we take the C–C bond length as 0.14 nm, the C–N length as 0.136 nm and the length of the phenyl ring as 0.28 nm), there must be two ϕ–NH units (ϕ = phenyl) of the PANI chain in the repeat length:



However, because of the bending angle at the nitrogen (and the torsion angle between rings), as sketched in *Figure 1*, the *c*-axis repeat length is 0.716 nm. The arcs in the c^* direction of the diffraction patterns are, therefore, consistently indexed as $\pm(0\,0\,2)$ reflections.

The periodic diffraction spots along the equatorial line, indicated by b^* in *Figure 4a*, give the *d* spacing of 1.791 nm. This is the *b*-axis lattice parameter of the crystallites. One would expect that *b* would be approximately the length of the DBSA molecule, and that the DBSA molecules would serve as spacers between the PANI chains within the structure. This is illustrated schematically in *Figure 1a*, where the *c* axis is defined as above along the PANI chain direction, while the interchain spacing, determined by the DBSA molecule, gives the *d* spacing along the *b* axis. We can roughly estimate the length of a molecule of DBSA from the chemical structure:



Taking the C–C bond length as 0.14 nm and assuming that the C–C chain forms the standard zigzag shape with dihedral angle of 120°, then the length of the C–C chain segment is approximately 1.40 nm. The length of the benzene ring is 0.28 nm[9] and that of the O–S–C segment is 0.30 nm[13]. By arranging the structure of the DBSA with respect to the PANI chain as sketched in *Figure 1*, one can accommodate the DBSA within the unit cell with a molecular length between polyaniline main chains of 1.791 nm, i.e. consistent with the measured *d* spacing.

The electron diffraction pattern obtained from selected segments of the fibrils gives additional information, as shown in *Figure 4b*. The arc reflections along the equatorial line indicate two repeat periods. One (along the b^* direction in the diffraction pattern and indicated by small arrows) corresponds to a *d* spacing of 1.791 nm, defined above as the *b*-axis spacing. The other (indicated by larger arrows) corresponds to a *d* spacing of 0.589 nm. We consider this period to be $a/2$ as a result of *n*-glide symmetry operations in the crystal (i.e. a diagonal glide in the *ac* plane, $n = a + c$ glide, resulting in a *n*-glide plane). This conclusion implies that the crystallites have random orientation in the plane transverse to the *c* axis. Thus, the $hk0$ reflections (e.g. both $0k0$ and $h00$) can be expected to appear in the diffraction pattern in the equatorial direction.

Figure 4d is the diffraction pattern of the PANI base. The emeraldine salt fibrils on gold grids (treated as described above) were reduced to the base form by immersion of the grids in 10% NH_4OH aqueous solution for 5 h. Similar arcs are seen along c^* as from the PANI–DBSA salt (*Figures 4a* and *4b*); the *d* spacing yields $c = 0.756$ nm. Only one blurred spot can be resolved on each side of the original PANI–DBSA spot in the equatorial direction. This reflection gives a *d* spacing of 0.575 nm. It is reasonable to consider that the blurred spots result from two superimposed reflections, $\pm(0\,1\,0)$ and $\pm(2\,0\,0)$, on each side of the original spot. With this assumption, the parameters of PANI base are $a = 1.134$ nm, $b = 0.575$ nm and $c = 0.756$ nm.

Table 1 Comparison of diffraction data for the emeraldine base (EB)

	Present work	Ref. 7
Sample	PANI–DBSA fibrils deprotonated to base form	EB film (EB-II) cast from *N*-methyl pyrrolidinone and drawn to $\lambda = 3$
Diffraction method	Electron diffraction from segments of fibrils (dimensions ~1 mm)	X-ray diffraction from tensile drawn films
Lattice parameters (nm)	$a = 1.178$ $b = 0.575$ $c = 0.768$	$a = 0.765$ $b = 0.575$ $c = 1.040$

Table 2 Interplanar spacings, Miller indexes and visually estimated intensities of observed reflections for PANI–DBSA fibrils

Reflections	d_0	d_c	*hkl*	Intensity
1	8.95	8.95	020	m
2	5.94(broad)	5.89	200	s
		5.97	030	
		5.60	210	
3	4.50(broad)	4.48	040	m
		4.92	220	
		4.19	230	
4	3.50	3.58	050	vw
5	3.00	2.99	060	w
		2.99	410	
6	3.58	3.58	002	vs
		3.51	012	
7	3.32	3.32	022	m
8	2.80	2.80	042	vw

These data can be compared with the lattice parameters for the emeraldine base (EB-II)[7,10]; the sample preparation, the diffraction method and the lattice parameters are listed in *Table 1*. As seen in the last row of *Table 1*, the lattice parameters obtained from the electron diffraction data are consistent with those of EB-II[7], if the *a* and *c* parameters are interchanged. Comparing the diffraction patterns of *Figure 4d* with those of ref. 7 for EB-II indicates a higher degree of orientation of the polymer chains in *Figure 4d*. In *Figure 4d* the $\pm(0\,0\,2)$ reflections appear as small arcs, indicating an order parameter $f \approx 0.96$ for the crystallites in the fibrils. In ref. 7, the diffraction intensity distribution forms continuous halos, implying a much smaller orientational order parameter than obtained from the fibrils (see *Figure 4*). Thus, the assignment of the *a*-axis and *c*-axis lattice parameters from the electron diffraction data appears to be more reliable.

X-ray diffraction data for the base form of polyaniline were also given in ref. 5. Using the lattice parameters defined above (as assigned by the electron diffraction data), one can account for all the diffraction peaks, providing further confirmation for the unit cell.

It is well known from the chemistry of the protonation of PANI that one out of every two nitrogen atoms on the main chain is protonated with DBSA molecules associated only with the protonated nitrogen. Thus, we conclude that there are two PANI chains in the unit cell, as shown schematically in *Figures 1b* and *1c*. The resulting chain packing is similar to that found for poly(phenylene oxide) and poly(*p*-phenylene sulfide)[14,15]. *Figure 1b* is a projection in the *bc* plane, where the PANI chains (along *c*) and DBSA molecules (along *b*) are related by glide lines in the *c* direction. *Figure 1c* is a projection in the *ab* plane. The two chains in the unit cell can be seen; one

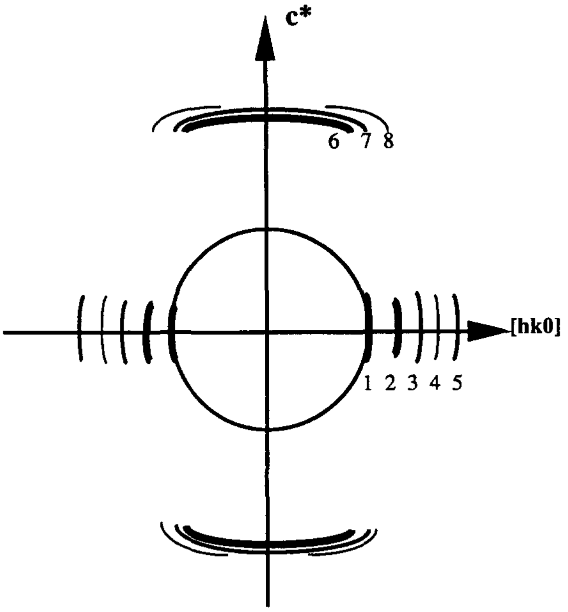


Figure 5 Schematic drawing of the diffraction pattern of *Figure 4b*, showing the indices of the inequivalent reflections listed in the first column of *Table 2*

is through the corner and the other through the centre.

With the structure as defined in *Figure 1*, the PANI–DBSA lattice parameters are the following: $a = 1.178$ nm, $b = 1.791$ nm and $c = 0.716$ nm. Because of the c^*-axis arcs ($f \approx 0.96$), it is impossible to discriminate between an orthorhombic and a monoclinic (with angles close to 90°) unit cell. Consequently, the parameters are given assuming an orthorhombic cell.

All the recorded reflections could be satisfactorily indexed consistent with the orthorhombic unit cell. *Table 2* summarizes the observed and calculated values of interplanar d spacings and their indices. The numbers in the first column correspond to non-equivalent reflections in the diffraction pattern of *Figure 4b*, as shown in the schematic drawing of *Figure 5*. The small discrepancies in the observed and the calculated interplanar d spacings are due to measurement error as a result of the relatively broad reflections (the observed d spacings are measured at the centres of the broadened diffraction spots).

As discussed above, there is a diagonal glide plane in the ac plane, i.e. $n = a + c$. As a result, the following reflections are absent: $(h00)$ with $h = 2n+1$ and $(00l)$ with $l = 2n+1$; there are no limitations on the $(0kl)$, $(hk0)$ reflections (see *Table 2*). The $(h0l)$ reflections with $h + l = 2n+1$ are systematically absent; no limitations were found for (hkl) reflections from our X-ray data. All of these results are consistent with the *Pmnm* space group. The structure sketched in *Figure 1* implies a crystallographic density of 1.12 g cm^{-3}, in agreement with the value of 1.14 g cm^{-3} obtained by the flotation method (in hexane and chloroform).

CONCLUSION

PANI–DBSA fibrils have been studied by TEM. The PANI–DBSA fibres are long and entangled with typical dimensions of 1 mm in length and 1 μm in width. The small crystallites in the fibres are oriented with c axis along the fibre. The crystal structure of the crystallites has been determined as orthorhombic with two PANI chains and two DBSA molecules per unit cell. The repeat unit of PANI is $-\phi-\mathrm{NH}-\phi-\mathrm{HN}^{\bullet +}-$, as shown earlier. The lattice parameters are $a = 1.178$ nm, $b = 1.791$ nm and $c = 0.716$ nm, and the calculated density of crystallites is 1.12 g cm^{-3}. The conditions limiting possible reflections are consistent with the *Pmnm* space group.

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