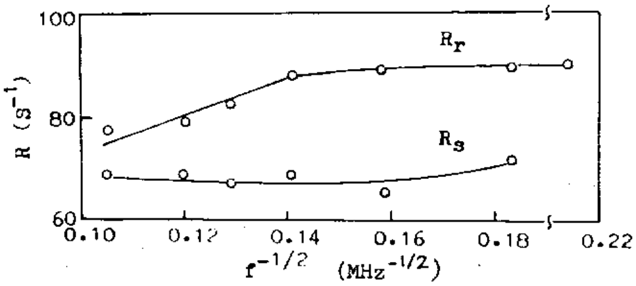

Figure 3 Relaxation rate *versus* $f^{-1/2}$ for sample CHP2.5

that $D_{\|}$ appears to have little relation to doping ratio unless it is very low.

From *Figure 3* it is seen that below 50 MHz the R_r *versus* $f^{-1/2}$ plot gradually approaches to a constant, characteristic of the interchain hopping of electrons. This suggests that the interchain hopping motion of electrons appears at low frequencies. The crossover between the intra- and interchain regimes occurs at $\omega = D_{\perp}$ (ref. 4). From the turning point of the R_r *versus* $f^{-1/2}$ plot, $D_{\perp}$ is estimated to be of the order of 10^8 rad s^{-1} in HCl-doped polyaniline. The ratio $D_{\|}/D_{\perp}$ can be used to characterize the anisotropy in the electron diffusive motion in conductive polymers. The $D_{\|}/D_{\perp}$ value for HCl-doped polyaniline is about 10^2, far lower than that in polyacetylene (ca. 10^6) (ref. 4). In other words, the anisotropy in electron diffusive motion is much smaller in the former than in the latter. So it is plausible to infer that the interchain hopping of electrons is an important factor for determining the conductive properties in doped polyaniline.

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X-ray scattering from crystalline polyaniline

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The results of wide angle X-ray scattering measurements from partially crystalline polyaniline are presented. The data indicate a relatively high degree of crystallinity of the (protonated) emeraldine salt form. It has been found that *partially crystalline* polyaniline can be prepared as the emeraldine salt either by direct synthesis or by precipitation from concentrated sulphuric acid. Although subsequent compensation reduces the crystallinity, the resulting emeraldine base shows X-ray reflections indicative of significant order.

(Keywords: wide angle X-ray scattering; polyaniline; crystallinity)

Introduction

Within the class of conducting polymers, polyaniline is unique in that its transport, optical and magnetic properties depend both on the extent to which it has been doped by charge transfer and on the extent of oxidation and protonation of the material[1–5]. The molecular structure of polyaniline can be described by two basic repeat units as shown in *Figure 1*[6]. The emeraldine base form is proposed to be an alternating copolymer $[(1\mathbf{A})_{0.5}(2\mathbf{A})_{0.5}]_n$, and the fully reduced leucoemeraldine form is the homopolymer $[1\mathbf{A}]_n$, where

$$(1\mathrm{A})=(\mathbf{B}-\mathrm{NH}-\mathbf{B}-\mathrm{NH}-)$$

and

$$(2\mathrm{A})=(\mathbf{B}-\mathrm{N}=\mathbf{Q}=\mathrm{N}-)$$

where **B** denotes a C_6H_4 ring in the benzenoid form and **Q** denotes a C_6H_4 ring in the quinoid form. The existence of one quinoid ring (out of four) in the emeraldine base has been well established in the literature[7–11]. Thus, an entire series of copolymers can be envisioned of the form $[(1\mathbf{A})_y(2\mathbf{A})_{1-y}]_n$ where $y=1$ is referred to as leucoemeraldine, and $y=0.5$ is the emeraldine base. From the point of view of structure, the use of $y=0.5$ for the emeraldine base assumes random positioning of the quinoid unit. If the alternating copolymer is ordered[7,10,11], the emeraldine base should be referred to as $[(1\mathbf{A})(2\mathbf{A})]_n$.

Although protonation of $[(1\mathbf{A})_{0.5}(2\mathbf{A})_{0.5}]_n$ to the emeraldine salt involves no change in the number of electrons[7–13], a major change in electronic structure is induced[3–5]. This has been attributed to a protonation-induced spin unpairing mechanism[14] which would lead to one unpaired electron per formula unit and the formation of a metallic polaron lattice[3–5,12,15] with a finite density of states at the Fermi level. Thus, by reaction with acid, the emeraldine base can be protonated to the corresponding salt

$$[1\mathrm{S}]^{\cdot}(\mathrm{A})_n=[-\mathbf{B}-\mathrm{NH}-\mathbf{B}-\mathrm{NH}^{+}-]_n(\mathrm{A}^{-})_n$$

where A^- is the counter ion (e.g. ClO_4^-, Cl^-, HSO_4^- etc.), and the $[\,]^{\cdot}$ denotes one unpaired electron per formula unit.

Although this conducting polymer is environmentally stable, scientific and technological progress have been impeded by limitations on material quality and processability; polyaniline has been reported as amor-

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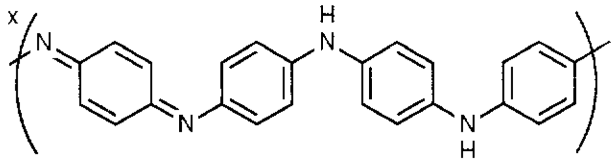

Figure 1 Molecular structure of the $[(1A)(2A)]_n$ emeraldine base

phous[16] with only limited short range order[17,18], intractable and largely insoluble in common solvents[19]. Complete solubility has been reported in *N*-methylpyrrolidinone and such solutions have been used for the preparation of films[20,21]. The recent discovery[22] that the emeraldine salt is completely and repeatedly soluble in sulphuric acid and that it can be recovered in partially crystalline form, without degradation, from solutions in sulphuric acid (by precipitation in water or methanol) has opened the way to a more complete characterization of the polymer, to studies directed toward the determination of the intrinsic properties of the ordered material, and to studies directed toward determination of the molecular packing and crystal structure.

In this initial communication preliminary results are presented of wide angle X-ray scattering measurements from partially crystalline polyaniline. The data indicate significant crystallinity of the (protonated) emeraldine salt and of the same material after compensation to the emeraldine base. It is found that *partially crystalline* polyaniline can be prepared as the emeraldine salt either by direct synthesis or by precipitation from concentrated sulphuric acid.

Experimental

Synthesis and sample preparation. Four samples were prepared for the X-ray diffraction studies:
1 polyaniline powder, $[1S]^{\cdot}(Cl)_n$, as-synthesized;
2 polyaniline film or powder precipitated in H_2O from a 12% w/w solution in H_2SO_4, $[1S]^{\cdot}(HSO_4^-)_n$;
3 polyaniline powder, $[1S]^{\cdot}(ClO_4^-)_n$, as-synthesized (using $HClO_4$ as protonic acid);
4 polyaniline powder in the emeraldine base form prepared by compensating material previously cast from concentrated sulphuric acid.

1 $[1S]^{\cdot}(Cl^-)_n$, as-synthesized. 23.0 g (0.11 mole) of $(NH_4)_2S_2O_8$ was dissolved in 250 ml of 1.5 M HCl aqueous solution; the mixture was added slowly (while stirring vigorously) into 250 ml of 1.5 M HCl solution containing 20 ml (0.22 mole) aniline previously cooled to 0°C in a temperature regulated bath. After all oxidant was added (over a period of 3.5 h), the reaction mixture was left stirring at 0°C for an additional 30 min. The precipitated polyaniline was filtered and then washed with distilled water until the washing liquid was completely colourless. In order to remove oligomers and other organic by-products, the precipitate was washed with methanol until the methanol solution was colourless. Finally, the material was washed twice with ethyl ether and subsequently dried at room temperature for 48 h in dynamic vacuum, until constant mass was reached. The degree of protonation of the resulting polyaniline salt after this washing procedure was estimated as about $y=0.17$ from elemental analysis (Cl/N). The electrical conductivity of a pressed pellet of resulting polyaniline was $1.2\,S\,cm^{-1}$ (four probe). The inherent viscosity at 25°C in 0.1% H_2SO_4 solution (w/w) was $1.17\,dl\,g^{-1}$.

2 $[1S]^{\cdot}(HSO_4^-)_n$. 23.0 g (0.11 mole) of $(NH_4)_2S_2O_8$ was dissolved in 50 ml of distilled water and added slowly into 200 ml distilled water that contained 20 ml (0.22 mole) aniline and 25 ml HCl solution (35%) cooled to 0°C in an ice bath. The final concentration of HCl in the reaction mixture was about 1.2 M. After all oxidant was added (over a period of 1 h) the reaction mixture was left stirring at 0°C for 23 h. The recovering procedure was exactly the same as sample 1. The electrical conductivity of a pressed pellet of resulting polyaniline was $2.7\,S\,cm^{-1}$ (four probe). The inherent viscosity in 0.1% (w/w) H_2SO_4 solution was $0.90\,dl\,g^{-1}$.

To obtain a film of $[1S]^{\cdot}(HSO_4^-)_n$, 0.5 g of the $[1S]^{\cdot}(Cl^-)_n$, as-synthesized in the previous paragraph was dissolved in 2.0 ml 96% H_2SO_4. After allowing the mixture to stand overnight (to obtain a homogeneous solution), the resulting viscous solution was spread and pressed between two glass slides. This 'sandwich' was left in air for 2 days during which the material slowly precipitated due to the penetration of moisture from the atmosphere. After precipitation was complete, the 'sandwich' was put into water, and the polyaniline film removed from the glass slides. The resulting film was washed several times with distilled water and methanol and dried in a dynamic vacuum at room temperature until it reached a constant mass.

For comparison, a powder sample was also prepared. Concentrated polyaniline solution (prepared as in the case of the film) was placed in a vial with a plastic cap and left in the air for about 1 month. During this period the polyaniline in the vial precipitated completely due to very slow penetration of moisture from the atmosphere. The washing procedure was the same as described for the film.

3 $[1S]^{\cdot}(ClO_4^-)_n$. Polyaniline perchlorate salt was prepared following the method described for sample 1 using 1.5 M $HClO_4$ solution instead of HCl. The electrical conductivity of pressed pellet was $4.4\,S\,cm^{-1}$ and inherent viscosity of the resulting polyaniline salt in 0.1% H_2SO_4 was $0.45\,dl\,g^{-1}$.

4 Polyemeraldine base film. Polyaniline salt film prepared as described for sample 2 was put in 29.7% aqueous NH_4OH solution for 30 min to achieve complete compensation. The resulting film was washed carefully several times by distilled water and put between two glass slides in air for 1 day for mild drying, followed by thorough drying in dynamic vacuum at room temperature for 24 h.

X-ray measurements. The Cu K_α radiation (line-focus) was provided by a 12 kW (60 kV at 200 mA) Rigaku rotating anode X-ray source. A flat highly oriented pyrolitic graphite crystal was used as the monochromator. The X-ray scattering instrumentation utilized a Huber 430/440 goniometer, which allows independent horizontal rotations of the sample and the Na(Tl) scintillation detector with angular resolution of 0.001°. The X-ray beam path was filled with He gas to reduce the air scattering.

Each sample (film or pellet) was placed in a thin steel pinholed sample holder for transmission X-ray scattering scans. The error caused by the thickness of the sample (typically less than 1 mm) was less than 0.1°.

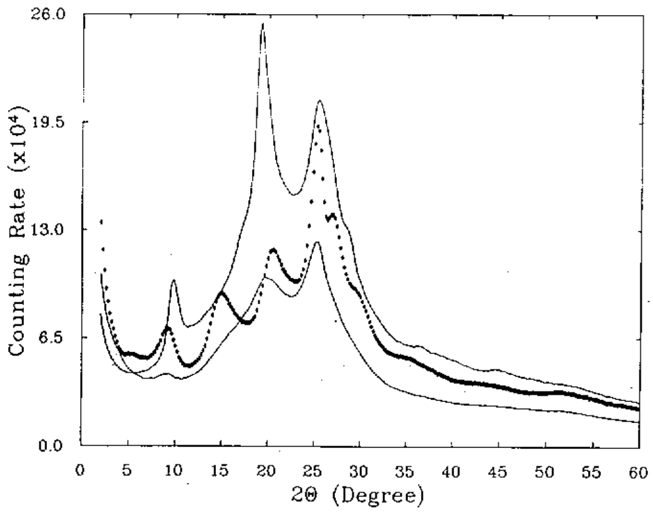

Figure 2 X-ray scans for: upper ——, $[1S]^{\cdot}(HSO_4^-)_n$; ◇◇◇, $[1S]^{\cdot}(Cl^-)_n$; lower ——, $[1S]^{\cdot}(ClO_4^-)_n$. For the upper curve, the counting rate is counts per 5 min interval; for the other two curves, the counting rate is counts per 4 min interval

Results and discussion

Polyaniline (emeraldine salt) was recovered in *partially crystalline* form from solutions in sulphuric acid[22]. This is demonstrated by the wide-angle X-ray diffraction pattern of such a polyaniline film, shown as the upper solid curve in *Figure 2*. Essentially identical data were obtained by X-ray scans from the film and powder samples. In addition, we found that the as-synthesized emeraldine salts, $[1S]^{\cdot}(Cl^-)_n$ (dotted curve) and $[1S]^{\cdot}(ClO_4^-)_n$ (lower solid curve), are partially crystalline. The data indicate that the $[1S]^{\cdot}(HSO_4^-)_n$ samples and the $[1S]^{\cdot}(Cl^-)_n$ sample are more highly crystalline than the $[1S]^{\cdot}(ClO_4^-)_n$ sample.

The intensity of the various reflections and their clear definition above the background amorphous scattering indicate that the $[1S]^{\cdot}(A^-)_n$ materials have significant crystallinity. For the $[1S]^{\cdot}(HSO_4^-)_n$ and $[1S]^{\cdot}(Cl^-)_n$ samples, as many as eight reflections can be identified. The relatively narrow widths of the diffraction peaks (full width at half maximum as narrow as approximately 1°) indicate relatively long range structure coherence.

Figure 3 compares the corresponding wide angle X-ray scans for the $[1S]^{\cdot}$ material (as precipitated from sulphuric acid) and the emeraldine base prepared by carefully compensating the same material by exposure to aqueous ammonia solution. Although compensation reduces the crystallinity, the resulting emeraldine base shows X-ray reflections which clearly indicate structural order.

Previous X-ray scattering studies by Wang *et al.*[23] resulted in the conclusion that the normal 1,4-coupled polyaniline shows only a few percent crystallinity. Significant crystallinity (>10%) was found[23] only when the polymerization was carried out in dilute acid solution (<0.3 M). Under these conditions, Wang *et al.*[23] conclude that there is significant head-to-head content (i.e. similar to poly-*p*-phenylenediamine). Indeed, their X-ray scans[23] are distinctly different from those reported here; for example, the low angle reflection reported by Wang *et al.* is at $2\theta \approx 6°$, whereas that shown in *Figure 2* is at $2\theta \approx 10°$, indicating a major difference in *d*-spacing. Ginder *et al.*[17] and Zuo *et al.*[18] state that preliminary diffraction experiments indicate that the protonated polymer has "only limited short range order". In contrast, the results shown in *Figures 2* and *3* demonstrate that for the conducting emeraldine salts, relatively high crystallinity with moderate coherence lengths can be achieved in material synthesized under conditions which yield high molecular weight[22] with head-to-tail polymerization[24].

Attempts to establish the details of the interchain packing and crystal structure through comparison of the calculated structure factors with the data in *Figures 2* and *3* are currently underway. However, some more general aspects of the structure can be inferred directly from the data. Initial diffraction patterns[22] obtained from emeraldine salt fibres with modest chain alignment have established that the reflection at $2\theta \approx 10°$ arises from scattering with momentum transfer along the orientation direction and hence approximately parallel to the polymer chains, whereas the two principal reflections (near $2\theta \approx 20°$ and 26°) involve momentum transfer, and thus periodicity, perpendicular to the chain direction.

The coherence lengths, ζ, parallel and perpendicular to the chains (based on the narrowest lines at $2\theta \approx 10°$ and 19°, respectively) are comparable. From the Scherrer formula,

$$\zeta \approx 2\pi\lambda/\delta(2\theta)$$

where $\delta(2\theta)$ is the full width at half-maximum, we find $\zeta \approx 10$ nm.

The positions of the diffraction peaks (and their linewidths) vary with changes in the counter-ion and upon compensation to the emeraldine base, indicative of different interchain packing and consistent with the different sizes of the counter-ions. In all cases, however, we observe the relatively narrow reflection at $2\theta \approx 10°$ which arises from scattering with momentum transfer approximately parallel to the polyaniline chains. In the emeraldine base, the structural coherence length along the chain direction remains comparable to that in the salt (as inferred from the low angle reflection), whereas the interchain coherence is definitely reduced by compensation and the subsequent removal of the $(NH_4^+A^-)$ salt.

The similarities between the molecular structure of the emeraldine base and those of poly(*p*-phenylene sulphide)[25], poly(*p*-phenylene oxide)[26], and even poly(*p*-phenylene terephthalamide)[27] suggest that a similar interchain packing might be expected. Indeed, the two strongest equatorial peaks in *Figure 3* (at $2\theta = 19.5°$ and

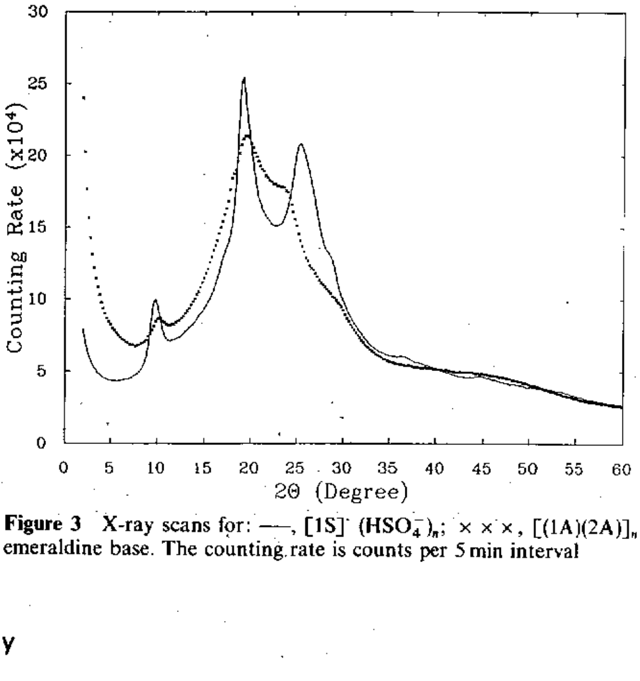

Figure 3 X-ray scans for: ——, $[1S]^{\cdot}(HSO_4^-)_n$; × × ×, $[(1A)(2A)]_n$ emeraldine base. The counting rate is counts per 5 min interval

Table 1 Summary of the 10° reflection data

	2θ(°)	d(nm)
$[(1A)(2A)]n$ base	10.3	0.86
$[1S]^{\cdot}(HSO_4^-)n$	9.7	0.91
$[1S]^{\cdot}(Cl^-)n$	9.1	0.98
$[1S]^{\cdot}(ClO_4^-)n$	9.0	0.98

$2\theta = 22.8°$) correspond to the similar peaks observed in all three materials. However, the low angle reflection (2θ near 10°) is not seen in the other polymers.

As would be expected from the simple protonation of the macromolecular structure, the repeat unit along c^* should be similar in the conducting $[1S]^{\cdot}(A^-)_n$ form and in the compensated $[(1A)_{0.5}(2A)_{0.5}]_n$ emeraldine base. There are clear shifts in the low angle reflection, however, corresponding to a repeat length increase from 0.859 nm in the $[(1A)(2A)]_n$ emeraldine base to 0.98 nm in the $[1S]^{\cdot}(Cl^-)_n$ salt. These are summarized in *Table 1*.

Conclusion

We have demonstrated through wide angle X-ray diffraction scans that polyaniline is partially crystalline in the $[1S]^{\cdot}(A^-)_n$ metallic emeraldine salt form. The observed periodicity along the chain direction corresponds to a repeat length of 0.98 nm, consistent with the structure proposed for the $[1S]^{\cdot}$ polymer chain. The X-ray reflection linewidths imply long range order with a coherence length of approximately 10 nm. Although compensation reduces the crystallinity, when carefully prepared by exposure to aqueous ammonia solutions (and subsequently thoroughly washed) the resulting emeraldine base also shows X-ray reflections indicative of significant order. Calculations of the structure factor directed toward a more complete analysis of the crystal structure, molecular packing and degree of crystallinity are underway.

The partial crystallinity of polyaniline (with relatively narrow and well defined diffraction peaks) was reported for polymer precipitated from concentrated sulphuric acid[22]. Surprisingly, and in contrast to earlier reports[16,17,23], it was found that polyaniline is also partially crystalline (with relatively long structural coherence lengths) as-synthesized in the emeraldine salt form, and even after compensation.

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